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Pacific Northwest National Laboratory 300 Area Facility Liquid Effluent Monitoring: 1994 and 1995 Field Tests

R. G. Riley
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Prepared for the U.S. Department of Energy
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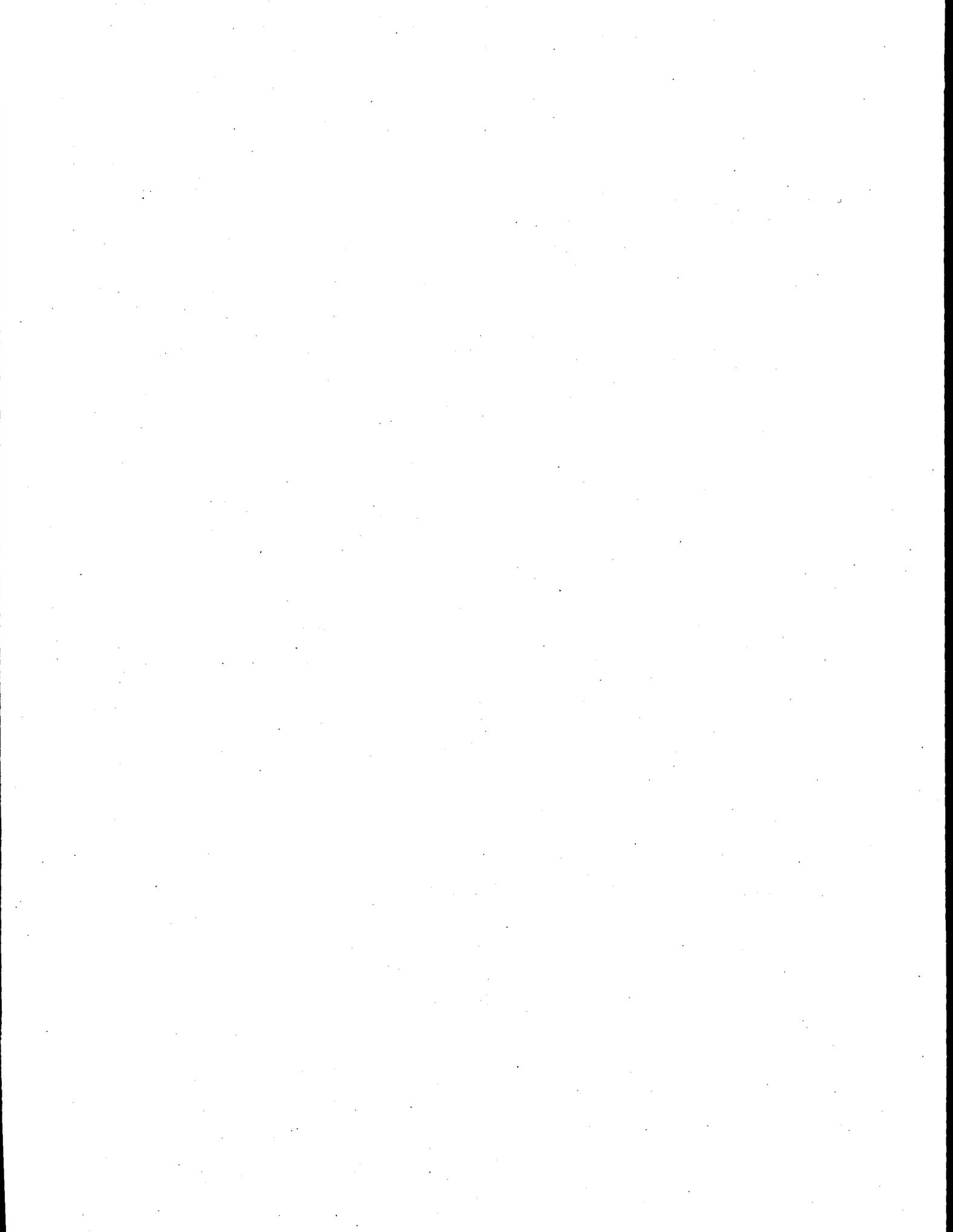
Abstract

Pacific Northwest National Laboratory Effluent Management Services manages liquid waste streams from some of the 300 Area buildings on the Hanford Site near Richland, Washington, to ensure liquid discharges to the Columbia River are in compliance with permit requirements. The buildings are owned by the U.S. Department of Energy and operated by Pacific Northwest National Laboratory. In fiscal year (FY) 1994 and FY 1995, three field tests were conducted to gather information that could be used to 1) increase the understanding of 300 Area building liquid waste streams based on the characterization and monitoring data collected during calendar year (CY) 1994 and CY 1995 and 2) establish improved methods for evaluating facility releases.

The three field tests were 1) an evaluation of a continuous monitoring/event-triggered sampling system, 2) a volatile organic compound hold-time study, and 3) an investigation of the dilution and retention properties of the 300 Area process sewer. The results from the first field test showed that future characterization and monitoring of 300 Area facility liquid waste streams could benefit significantly from augmenting continuous monitoring with event-triggered sampling. Current continuous-monitoring practices (i.e., monitoring of pH, conductivity, and flow) cannot detect discharges of organic pollutants. Effluent control effectiveness would be enhanced by incorporating a continuous total organic carbon analyzer in the system to detect events involving releases of organic compounds.

In the second field test, sample hold times were shown to have a significant effect on volatile organic compound data. Samples analyzed in the field within 1 hour of collection generally had 1.5 to 3 times higher volatile organic compound concentrations than those analyzed 1.5 to 4 weeks later at on-site and off-site laboratories, respectively. The number of volatile organic compounds detected also decreased with increasing hold times. It was concluded that CY 1994 and CY 1995 volatile organic compound data from the routine monitoring of 300 Area facility waste streams are biased low and probably include several false nondetects. However, the presence of this bias did not result in changes in the interpretation of 1994 and 1995 routine-monitoring volatile organic compound data particularly at end-of-pipe.

The third test revealed that pollutant transport and dilution properties of the 300 Area process sewer were highly dependent on waste stream flow rates and the mechanical action of sumps. Where present, the action of sumps had the greatest impact on contaminant clearance times. In the absence of sump activity, the waste stream flow rate was the controlling factor. Average dilution factors ranging from 9.7 to 524 were shown to be valuable in predicting the impact of facility releases on end-of-pipe effluent contaminant concentrations. Comparison of the behavior of a fluorescent dye with that of hexone (a common pollutant in facility waste streams) showed that the dye provides a conservative estimate of real waste stream pollutant behavior.



Summary

Pacific Northwest National Laboratory Effluent Management Services manages liquid waste streams from some of the 300 Area buildings on the Hanford Site near Richland, Washington, to ensure liquid discharges to the Columbia River are in compliance with permit requirements. The buildings are owned by the U.S. Department of Energy and operated by Pacific Northwest National Laboratory. In calendar year (CY) 1994 and CY 1995, the Laboratory monitored liquid effluent pH, conductivity, and flow at primary buildings and collected composite samples once or twice a month for chemical and radiological analysis. Data from the sample analyses have been summarized in the Laboratory's Liquid Waste Certification Plan, which is required by the 300 Area Treated Effluent Disposal Facility Waste Certification Program. The Treated Effluent Disposal Facility treats the combined effluent before discharging it to the Columbia River.

In fiscal year (FY) 1994 and FY 1995, three field tests were conducted to gather information that could be used to 1) increase the understanding of 300 Area building liquid waste streams based on the characterization and monitoring data collected during CY 1994 and CY 1995 and 2) establish improved methods for evaluating facility releases. In the first field test, the process sewer stream from the 331 Building, a life sciences laboratory, was monitored continuously for pH, conductivity, and flow rate for a 10-day period in July 1995 and a 2-week period in late August and early September 1995. These data were supplemented by similar data collected during a 2-week period in February 1995. All of the continuous monitoring data were used to detect and evaluate event patterns and their frequencies of occurrence. Operations staff from the 331 Building were also interviewed to obtain information on process and discharge practices. This information was related to data collected during the test. In addition, approximately 350 samples were collected from the waste stream during events. Sampling was triggered by high or low pH and/or elevated conductivity of the waste stream. Selected samples were analyzed for anions, metals, and volatile organic compounds. These data were used to assist interpretation of continuous monitoring information and to compare the chemistry of the waste stream during events to CY 1994 and CY 1995 routine-monitoring data.

During the second field test, grab samples were collected from the 331 Building waste stream in late August/early September 1995, and the samples were split for subsequent volatile organic compound analyses in the field, at Pacific Northwest National Laboratory (the on-site laboratory), and at an off-site commercial laboratory. In-field measurements were made within 1 hour of collection using a portable gas chromatograph/mass spectrometer. The remaining split samples were preserved and transported to the on-site and off-site laboratories. On-site analyses were performed within 10 to 14 days, and off-site analyses were performed within 23 to 27 days of collection. These three data sets were then compared to assess the effects of hold times on interpretation of laboratory-acquired volatile organic compound data.

The third field test consisted of a series of waste stream fluorescent dye releases, in the absence or presence of an organic contaminant simulant, to a facility sump or sink. These releases were performed during FY 1994 and FY 1995 to estimate transit and clearance times and average dilution during transit from selected 300 Area facilities to the end-of-pipe. Dyes were monitored in real-time near the point of release and at the end-of-pipe using field-portable fluorometers. The organic contaminant simulant hexone (i.e., methyl isobutyl ketone) was tracked by collecting grab samples of the

waste stream when the dye was detected. Subsequently, the samples were analyzed by gas chromatography/mass spectrometry. Results from these tests were used to establish relationships among the chemistry of facility effluents, the physical properties of facility waste streams, and the chemistry of the waste stream at end-of-pipe.

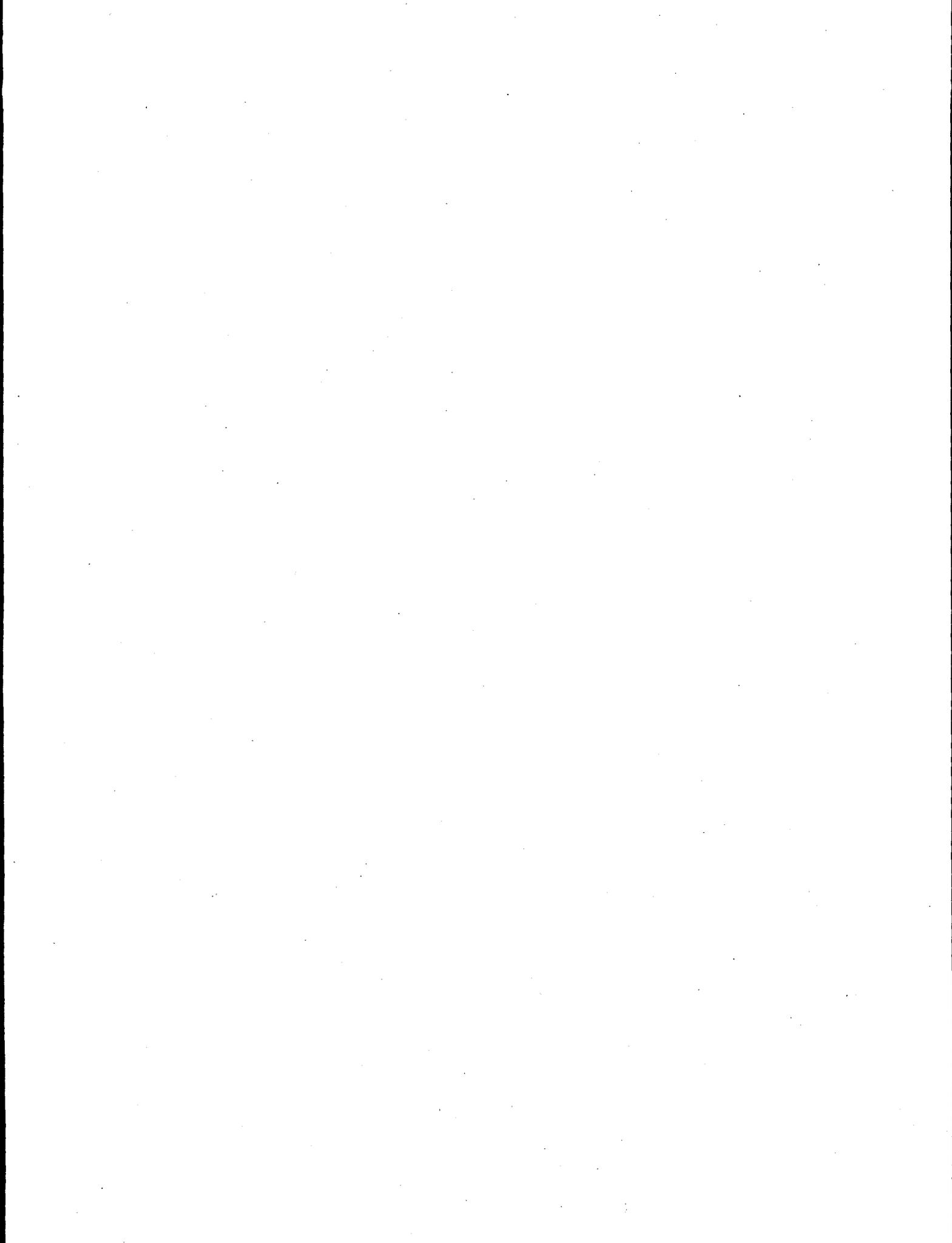
Almost all events detected by continuous monitoring of pH, conductivity, and flow at 331 Building occurred during regular work hours. Two patterns of waste stream events that appeared to occur on a frequent basis were identified. One pattern appeared to have a chemistry consistent with cage and glass washing activities, while the other may be associated with ongoing life sciences research. Event samples often contained contaminant levels one to two orders of magnitude above levels observed in CY 1994 and CY 1995 routine-monitoring samples. However, these elevated concentrations were predicted to be less than Treated Effluent Disposal Facility waste acceptance criteria or U.S. Environmental Protection Agency maximum contaminant levels at end-of-pipe. The CY 1994 and CY 1995 routine monitoring at end-of-pipe indicated occasional releases of contaminants (e.g., nitrate) at levels significantly above their maximum contaminant levels. These levels likely resulted from releases containing contaminant levels significantly above those observed in the field test (i.e., from concentrated releases from one or more 300 Area facilities). Events resulting in releases of organic compounds may go undetected utilizing the current continuous monitoring capability. For example, in the first field test, instances of event samples containing high levels of acetone and isopropyl alcohol were shown to be associated with normal pH and conductivity responses.

It is well known that sample hold times (i.e., time from sample collection to sample analysis) can significantly affect volatile organic compound data quality. However, the magnitude of the effect on 1994 and 1995 routine-monitoring data had not been quantified. The results of the hold-time study suggest that volatile organic compound data from CY 1994 and CY 1995 routine monitoring of facility waste streams are probably biased low by a factor of 1.5 to 3.0. As a consequence, routine-monitoring data probably underestimates the number of times the concentrations of volatile organic compounds in liquid effluent samples were greater than Treated Effluent Disposal Facility waste acceptance criteria. However, when accounted for, this bias did not result in any changes in the interpretation of 1994 and 1995 volatile organic compound data at end-of-pipe. Test results indicated more volatile organic compounds were detected in samples analyzed in the field than by on-site and off-site laboratory analyses. Therefore, CY 1994 and CY 1995 routine monitoring of facility effluents probably failed to detect several occurrences of volatile organic compounds due to analyte losses. However, the inability to detect these compounds in routine-monitoring samples collected at end-of-pipe would not have resulted in missed exceedances of Treated Effluent Disposal Facility waste acceptance criteria.

Concentrations, transit times, and clearance times for contaminants at end-of-pipe were highly dependent on waste stream flow rates and the mechanical action of sumps. Where present, sump action increased contaminant clearance times by several hours. In the absence of sump activity, the waste stream flow rate was the controlling factor. Dilution factors were shown to be valuable for predicting the impact of facility releases at end-of-pipe. For example, it was estimated that four contaminants released from 331 Building during routine monitored events at levels above Treated Effluent Disposal Facility waste acceptance criteria or U.S. Environmental Protection Agency maximum contaminant levels would not have exceeded those levels at end-of-pipe. The effect of waste stream dilution of a contaminant (i.e., dilution that occurs between a facility release point and end-of-pipe) should be considered significant when calculating and assessing inventory release quantities associated with

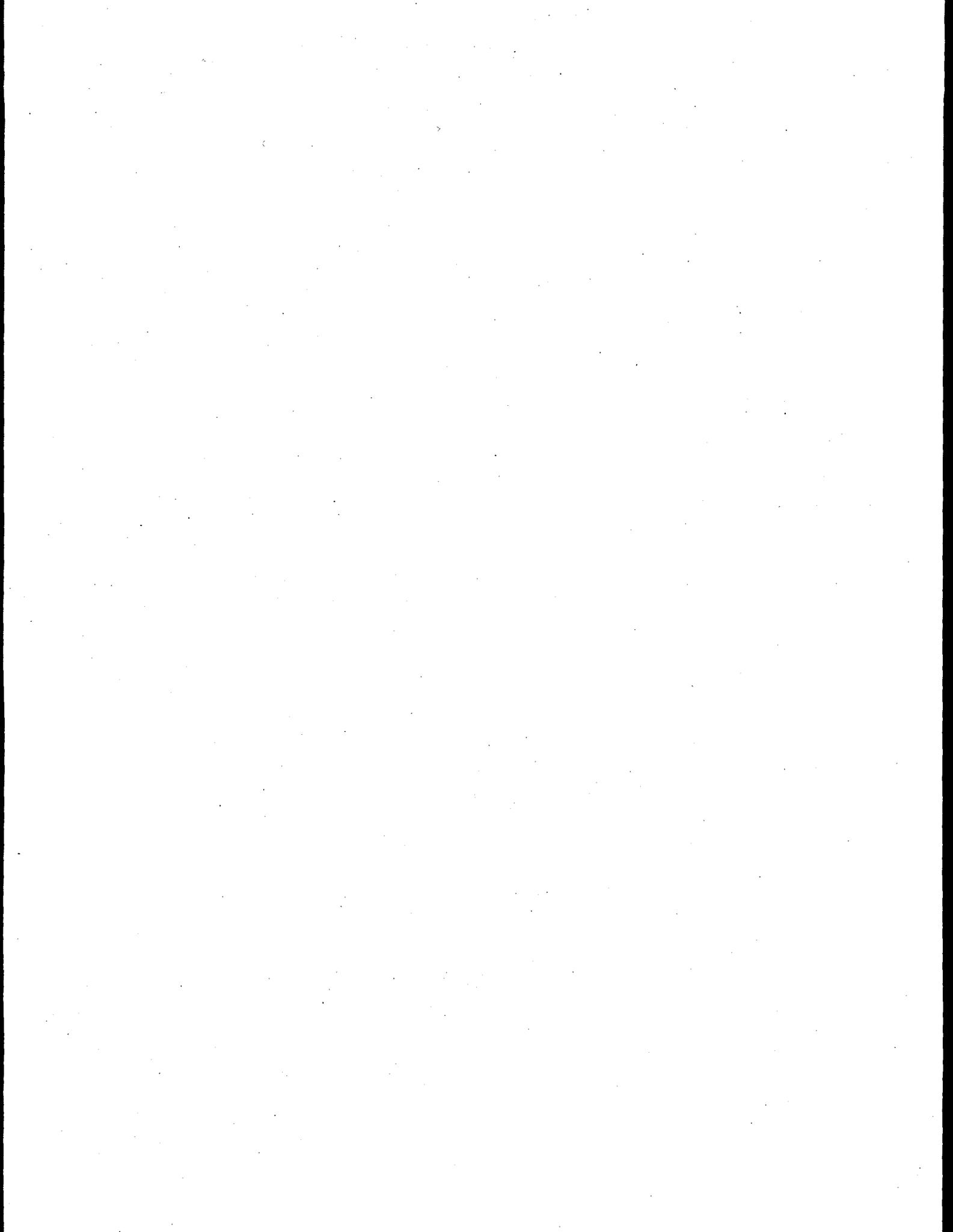
hazardous chemical and radionuclide spills to facility process sewers. Comparison of the behavior of a fluorescent dye with that of hexone showed that the dye provided a conservative estimate of real waste stream organic contaminant behavior at end-of-pipe.

Continuous monitoring for organic carbon would detect events that include organic chemical releases. Incorporation of event-triggered, automated sampling could be used to focus sample collection and limit analyses to those samples most likely to 1) contain significantly elevated levels of contaminants (i.e., those which might exceed Treated Effluent Disposal Facility waste acceptance criteria or U.S. Environmental Protection Agency maximum contaminant levels) and 2) show failure of facility administrative control practices. Additional dye tests on facility effluents could provide additional information such that end-of-pipe impacts from discharges from each 300 Area facility could be further estimated. Sample hold times limited to less than 10 days could minimize volatile organic compound losses in on-site and off-site analyses. On-site and/or off-site analyses could be augmented by selected field analyses. Alternatively, data should be interpreted realizing that not all volatile organic compounds may have been detected and the analyte concentrations in the waste streams may have been significantly higher than laboratory results indicate.



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Acronym List

CY	calendar year
EPA	U.S. Environmental Protection Agency
FY	fiscal year
GC/MS	gas chromatograph/mass spectrometer
MCL	maximum contaminant level (for drinking water)
MDL	method detection limit
TEDF	Treated Effluent Disposal Facility
VOC	volatile organic compound
WAC	waste acceptance criteria

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1.0 Introduction

The liquid effluent management task of the Effluent Management Project characterizes and monitors liquid waste streams from certain 300 Area buildings on the Hanford Site near Richland, Washington. The buildings are owned by the U.S. Department of Energy and operated by Pacific Northwest National Laboratory.^(a) The building liquid waste streams are combined and discharged at end-of-pipe to the Treated Effluent Disposal Facility (TEDF) where they are treated before being discharged to the Columbia River in accordance with a National Pollutant Discharge Elimination System Permit issued by the U.S. Environmental Protection Agency (EPA). In fiscal year (FY) 1994 and FY 1995, Pacific Northwest National Laboratory installed equipment to continuously measure liquid effluent pH, conductivity, and flow at some of these buildings. Automated samplers were also used at these same locations to obtain composite samples once or twice a month for chemical and radiological analyses. The characterization and monitoring data (Thompson et al. 1997, in press) are being used to support Pacific Northwest National Laboratory's Liquid Waste Certification Plan for 300 Area facilities in response to a TEDF Liquid Waste Certification Program.

With the exception of knowledge gained from interviews of staff regarding facility activities and operations, very little information was available at the onset of the program to design the routine sampling and analysis effort. Several limitations were recognized in the sample collection and analysis practices that were used for routine monitoring during FY 1994 and FY 1995. First, samples were composited over 24 hours, and collected once or twice a month, and therefore, each sample represented only a small fraction of the total waste stream discharged from one or a combination of all facilities. Moreover, because the samples were composited, they were less likely to capture the true chemistry (i.e., composition and concentration) of the waste stream if and when events were occurring. Second, collected samples were sent off-site for chemical analysis where hold times were contractually set to begin at the time of receipt by the contracting laboratory. While it was known that hold times biased volatile organic compound (VOC) data (i.e., low) generated over the calendar year (CY) 1994 through CY 1995 timeframe, the magnitude of the bias had not been quantified. Also unknown was whether all VOCs of interest and possibly present in field samples were being detected due to delay in analyses performed off-site. The VOC losses may occur during sample storage via several processes, including transfer through the vial's septum, microbial degradation, and chemical reactions. In principle, these mechanisms should be reduced or eliminated by acidifying the samples and storing them at low temperatures. A previous study on hold times has shown that in some cases water samples may be stored up to one year with little or no effect on VOC concentrations (Maskarinec et al. 1989).

Another limitation related to the interpretation of characterization and monitoring data was that the relationship between the chemistry of facility releases and the chemistry at end-of-pipe (where all of the waste streams were combined) was unknown. Without specific knowledge of the attenuation and retention properties of the sewer systems, it was difficult to evaluate the effects of facility releases on

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end-of-pipe pollutant composition. Understanding such relationships is important because end-of-pipe is the point at which influents to the TEDF are required to meet criteria established to ensure the facility can meet its permitted discharge limits.

This report describes the results and conclusions from three field tests that were performed during FY 1994 and FY 1995 at Buildings 320, 324, 331, and 3720, located in the Hanford Site's 300 Area (Figure 1.1). The findings of this report can be used as guidelines for improving the current approach to characterization and routine monitoring of facility liquid waste streams, which relies on continuous pH, conductivity, and flow data to supplement biweekly monitoring of TEDF's influent. This report can also be used to better interpret data acquired during CY 1994 and CY 1995 to characterize facility liquid effluent streams and to support current and future administrative control needs and practices in the 300 Area, including Pacific Northwest National Laboratory's Liquid Waste Certification Plan.

For the first two tests, Building 331 was selected because of its history of having a high level of event (i.e., pH and conductivity spikes) activity, the presence of multiple contaminant (i.e., anions, metals, and organic) discharges, and the ease and therefore lower cost of sampling its liquid waste stream. The Life Science Laboratory (331 Building) is designed primarily as a facility to support biological and environmental research and development. The building consists of laboratories designed for cellular, molecular, and biochemical research using plant and animal models and tissues, laboratories designed for the study of subsurface and airborne transport of radiological materials and other substances, as well as small animal quarters. Special facilities include a freshwater aquatic ecology laboratory that is provided with Columbia River or well water, a 50,000 Ci cobalt-60 irradiation facility, and a superconducting magnet facility for nuclear magnetic resonance studies.

1.1 Purpose

The purpose of the field tests was to 1) increase the understanding of 300 Area building liquid waste streams based on the characterization and monitoring data collected during CY 1994 and CY 1995 and 2) establish improved methods for evaluating facility releases.

1.2 Approach

In the first field test, 331 Building operations staff were interviewed to identify facility practices that may have contributed to significant deviations in parameters (i.e., pH, conductivity, and flow) routinely monitored in 331 Building wastewater discharges and specific process chemistry. The 331 Building process waste stream was then monitored continuously for pH, conductivity, and flow for a 10-day period in July 1995 (campaign 1), and a 2-week period in late August through early September 1995 (campaign 2). These data were supplemented by similar data collected during a 2-week period in February 1995. Data were evaluated to determine the type, duration, and frequency of occurrence of event patterns; the interrelationships and intensities of continuous monitoring parameters (i.e., pH, conductivity, and flow); and parameter settings required for triggering an automated sampler to collect event samples.

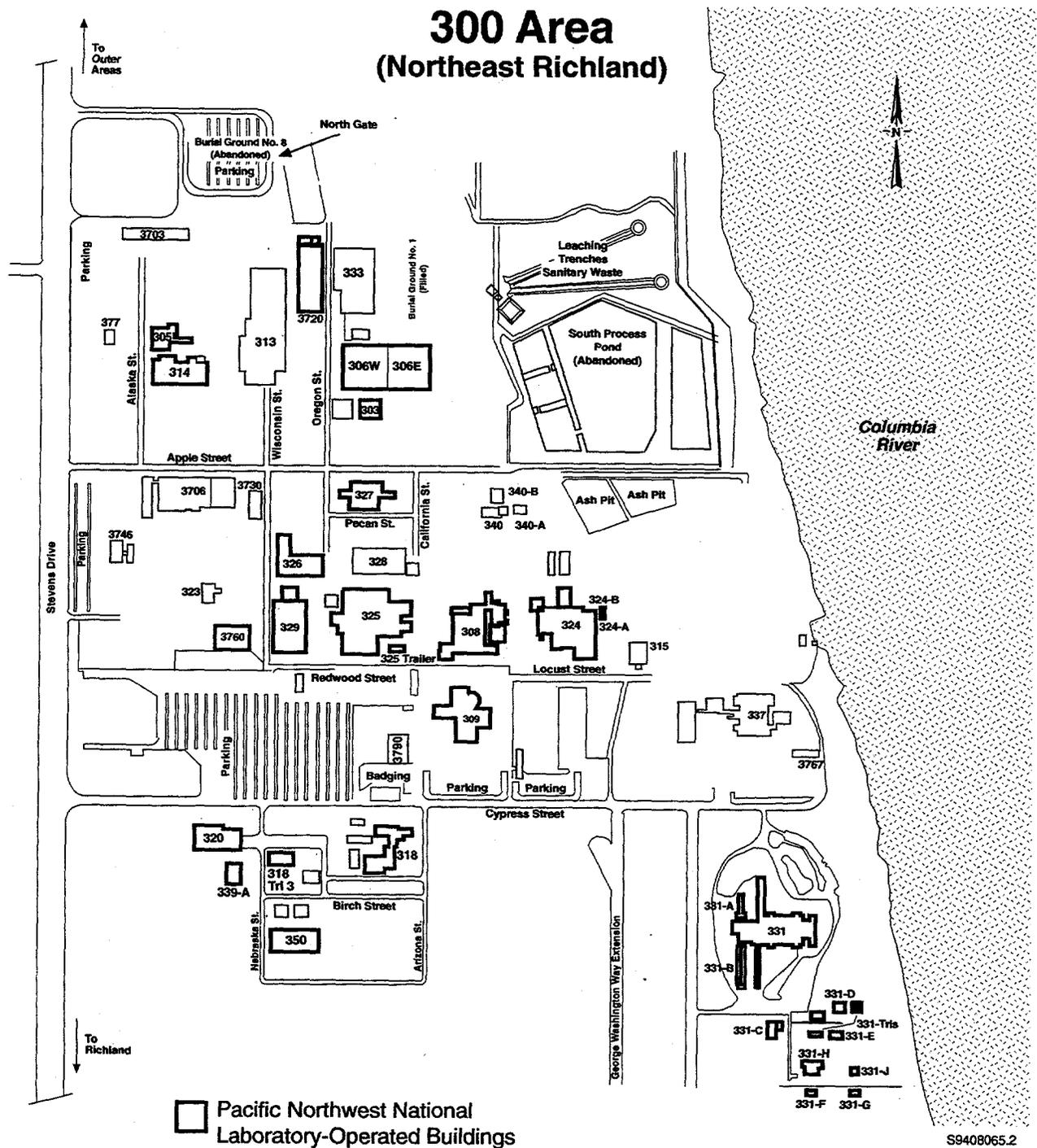


Figure 1.1. Location of Pacific Northwest National Laboratory-Operated Buildings in the 300 Area

Approximately 350 event-triggered samples were collected during the first field test. Sixty of the samples were analyzed at on-site and off-site laboratories for selected anions, metals, and VOCs. The analytical data were evaluated for elevated levels of contaminants based upon a predetermined set of criteria, that is, elevation above CY averages or maximums, TEDF waste acceptance criteria (WAC) or EPA maximum contaminant levels (MCLs). Qualitative comparisons were also made between event patterns and their chemistry.

In the second field test, twenty-five grab samples were collected at approximately 30-minute intervals, split, and analyzed in the field and at on-site and off-site laboratories for a selected set of VOCs. Field analyses were performed within 1 hour of sample collection, while on-site and off-site analyses were performed 10 to 14 and 23 to 27 days, respectively, after collection. Data from each set of analyses were compared (i.e., number of VOCs present in each sample and their associated concentrations) as a function of sample hold time to assess test data quality. Results of the test were used to assess the quality of CY 1994 and CY 1995 routine-monitoring VOC data.

In the third field test, a total of 35 dye releases (acid red #52 and rhodamine WT) into 331, 3720, 320, and 324 Building liquid waste streams were performed during CY 1994 and CY 1995. Dye behavior (i.e., arrival, transit and clearance times; concentration profiles) at facility release points and at end-of-pipe was determined from waste stream data collected continuously using fluorimeters. A mixture of rhodamine WT and hexone was released into the process sewer from a building sink as one additional component of the field test. Dye concentrations were monitored as described previously, and samples of the waste stream were collected at the release point and end-of-pipe for subsequent hexone analysis by the on-site laboratory. Estimates of dilution were calculated from pollutant data collected from facility release points and end-of-pipe. The value of dilution factors was demonstrated in their application to two facility contaminant release scenarios.

2.0 Background

For approximately 40 years, the Hanford Site's 300 Area was used as a research center in support of nuclear material for national defense needs. Activities in these facilities were primarily focussed on evaluating pilot-scale reactor fuel fabrication and separations processes. The Hanford Site's mission has evolved as has the mission of the 300 Area to include research in support of site waste management and environmental cleanup and the life sciences.

For many decades, chemically and radiologically contaminated wastewaters from activities in the 300 Area were discharged to ponds, trenches, and cribs (Riley and Zachara 1992). In 1989, an agreement was reached among the Washington State Department of Ecology, the EPA, and the U.S. Department of Energy, Richland Operations Office to eliminate process sewer discharges to the trenches. This was facilitated by the construction and operation (December 1994) of the TEDF in the 300 Area for treatment of 300 Area facility liquid waste to technology-based standards before discharging the effluent to the Columbia River.

Characterization data were needed to determine how well the 300 Area facilities could meet TEDF's planned WAC and to assess the effectiveness of facility administrative controls^(a) on releases to the process sewers. In response to this need, Pacific Northwest National Laboratory conducted characterization and routine monitoring of the liquid waste streams from eight facilities in the 300 Area from March 1994 through September 1995 (Riley et al. 1994; Riley et al. 1995). The monitoring was done using liquid effluent monitoring stations installed at each facility and at the confluence of all 300 Area process sewer streams (end-of-pipe). Monitored facilities were 320, 324, 325, 326, 327, 331, and 3720 Buildings. In addition, a portable sampler collected effluent from 306 Building. These buildings were chosen because they are the primary contributors of liquid waste to the process sewer or because they have the greatest potential to discharge hazardous materials. The monitoring stations included 1) samplers capable of obtaining grab and composite samples from the liquid waste stream and 2) equipment to continuously measure stream pH, conductivity, and flow. The sampling and analysis process consisted of collecting weekly to monthly 24-hour composite samples and analyzing the samples for general chemical and radiological parameters, anions, metals, and volatile and semivolatile organic compounds.

Late in 1995, an agreement was reached between Westinghouse Hanford Company (who operated TEDF), Pacific Northwest National Laboratory, and U.S. Department of Energy in which the Laboratory would prepare a Waste Certification Plan. This plan would replace the need to perform additional routine characterization and monitoring of Pacific Northwest National Laboratory building effluents. Westinghouse Hanford Company would continue to monitor the combined influent to all 300 Area facilities, and Pacific Northwest National Laboratory would continue to provide continuous data on pH, conductivity, and flow. Individual Pacific Northwest National Laboratory-operated facility samplers were placed in standby to address future facility-specific discharges when needed.

(a) Administrative controls are used at Pacific Northwest National Laboratory to ensure that wastes regulated as hazardous are not discharged to the sewer and that discharges either meet sewer criteria (e.g., TEDF WAC) or qualify for a waiver.

Field tests were designed and conducted in the summer of 1995 to 1) increase the understanding of 300 Area building liquid waste streams based on the characterization and monitoring data collected during CY 1994 and CY 1995 and 2) establish improved methods for evaluating facility releases.

3.0 Procedures

Field test plans were prepared and approved to conduct the field tests. The following procedures were implemented for sampling and data collection.

3.1 Event-Triggered Sampling System, Sample Collection, and Analysis

3.1.1 System Description

Event-triggered sampling was conducted using a portable wastewater sampler controlled by a measurement and control module (i.e., data logger). The control module collected and stored monitoring data from the pH, conductivity, and flow sensors located in the 331 Building effluent stream. Measurements were made from each device at 5-second intervals and stored as 1-minute averages. Figure 3.1 shows the general configuration of the sampling and monitoring system. Equipment comprising the system included the following:

- ISCO® Model 3700 portable sampler with 24 discrete 1-L bottles
- Campbell Scientific Inc. CR10 Measurement and Control Module (data logger)
- ISCO® Model 3240 variable gate flow meter
- Signet Model 9859 analog conductivity meter
- Signet Model 9030 digital pH meter.

3.1.2 Sample Collection and Analysis

The waste stream was continuously monitored for variations in pH, conductivity, and flow for approximately 30 days before conducting event-triggered sampling. Data collected during this time period was used to determine the normal operating baseline and the approximate frequency, duration, and magnitude of events (i.e., extreme variations in pH or conductivity) relative to the baseline. Trigger parameters and levels were then established for the collection of event samples.

Trigger parameters consisted of set values of changes in either the pH or conductivity of the waste stream. If the pH was above 8.0 or below 7.4, or if the conductivity was above 250 μ S, a signal was sent from the data logger to the sampler initiating the collection of a discrete 1-L sample. Once the sample was collected, the system began a 10-minute wait period to prevent the collection of multiple samples from a single event. Upon completion of the wait period, the system was again available to collect another discrete sample, up to a maximum of 24 samples per day.

Not every sample collected in a 24-hour period was selected for further chemical analysis. Some qualitative screening was performed in the field that led to selection of 60 samples for detailed

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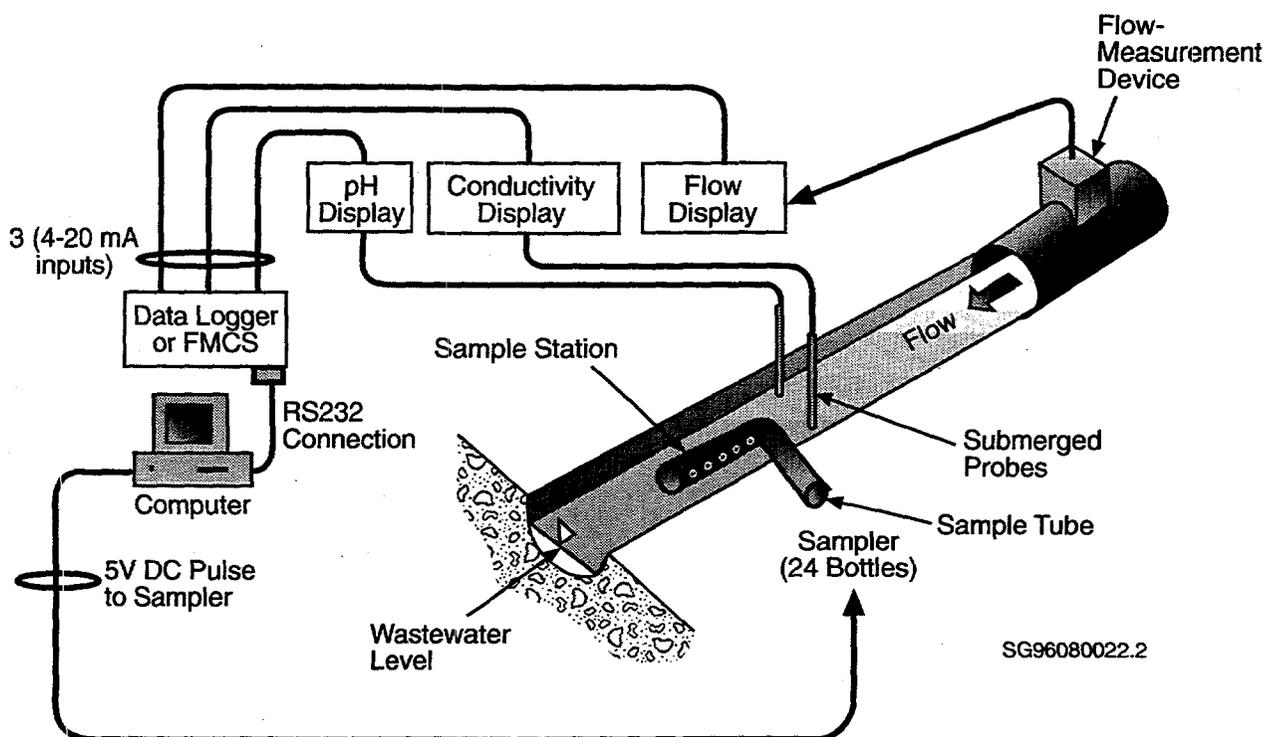


Figure 3.1. System Configuration for Continuous Monitoring of Waste Stream pH, Conductivity, and Flow

laboratory analysis. Samples with the largest changes in pH and conductivity response were highest priority among the 60 samples selected. Samples that had a similar pH and conductivity “signature” were next and were selected for comparison of individual event chemistries. Finally, samples that exhibited discoloration or high solids content were given lowest priority for detailed analysis.

3.2 Volatile Organic Compound Hold-Time Sampling and Analysis

3.2.1 Sample Collection and Preservation

Twenty-five samples were collected during September 7 through 11, 1995, for in-field, on-site, and off-site analysis of VOCs. Samples were obtained using a 10-ft (3.1-m) length of 1/4-in. (0.61-cm) stainless steel tubing connected to a positive-displacement pump. In general, samples were collected at approximately 30-minute intervals (i.e., no attempt was made to collect samples during periods of high or low pH or conductivity readings). The collection process consisted of 1) pumping 331 Building effluent into a 250-mL glass bottle until three bottle volumes of effluent had passed through the bottle, 2) removing the filled bottle from the pump line, 3) immediately pouring aliquots of the bottled wastewater into five separate (one field, one on-site, three off-site) 40-mL volatile organic analyte vials, and 4) tightly capping the vials.

Samples for on-site (Pacific Northwest National Laboratory) and off-site (commercial laboratory) analyses were preserved with hydrochloric acid and sodium thiosulfate and were transported in ice chests and stored in refrigerators. Table 3.1 lists the collection times and identifies where samples were analyzed. All of the samples were analyzed in the field and on-site. Based on the field results, 12 samples were selected for off-site analysis.

Table 3.1. Sample Collection Times and Analysis Locations

Sample ID	Date	Time	Field	On-Site	Off-Site
10	9-7-95	11:44	•	•	
11	9-7-95	12:18	•	•	
12	9-7-95	12:55	•	•	•
13	9-7-95	13:29	•	•	•
14	9-7-95	14:02	•	•	•
15	9-7-95	14:34	•	•	•
16	9-7-95	15:14	•	•	
17	9-8-95	10:27	•	•	•
18	9-8-95	11:03	•	•	•
19	9-8-95	11:52	•	•	•
20	9-8-95	12:21	•	•	
21	9-8-95	12:49	•	•	
22	9-8-95	13:52	•	•	
23	9-8-95	14:34	•	•	
24	9-8-95	15:01	•	•	•
25	9-11-95	09:45	•	•	
26	9-11-95	10:38	•	•	
27	9-11-95	11:09	•	•	•
28	9-11-95	11:40	•	•	
29	9-11-95	12:12	•	•	
30	9-11-95	13:23	•	•	•
31	9-11-95	13:55	•	•	•
32	9-11-95	14:26	•	•	•
33	9-11-95	14:57	•	•	
34	9-11-95	15:40	•	•	

3.2.2 Methodology for Volatile Organic Compound Analysis

Different gas chromatographic methods were used to analyze samples in the field, at the on-site laboratory, and at the off-site laboratory. Table 3.2 summarizes the key elements of each of the methods. Both the on-site and off-site laboratories used similar, approved EPA methods based on purge-and-trap sample preconcentration and a dual-detector system consisting of photoionization and electrolytic conductivity detectors. For most analytes, the method detection limits (MDLs) were approximately 0.07 $\mu\text{g/L}$ for the off-site laboratory and 0.5 $\mu\text{g/L}$ for the on-site laboratory. The field analyses were made using a headspace method performed on a Viking SpectraTrak portable gas chromatograph/mass spectrometer (GC/MS) system housed in the back of a Chevrolet® Suburban® (Figure 3.2). For maximum sensitivity, the GC/MS was operated in selected ion monitoring mode, and detection limits of approximately 0.3 $\mu\text{g/L}$ were determined for most analytes.

A comparison of the field and on-site methods' precision and accuracy was made by using each method to analyze a sample containing known concentrations of a mixture of 19 commercially available VOC standards. The sample was split and poured into six volatile organic analysis vials to enable triplicate determinations by each method. Simultaneous analyses of the sample splits were performed using the two methods approximately 2 hours after the sample was prepared. The results from the precision and accuracy evaluation of the field and on-site methods of analysis are summarized in Table 3.3. Field and on-site methods showed comparable performance (i.e., maximum bias within 10 to 15% and analytical precision of <4% in all cases for both methods).

Table 3.2. Comparison of Analytical Methods and Field-Test Hold Times

Location	Method	Detector	MDL ^(a) ($\mu\text{g/L}$)	Hold Times ^(b)
Field	Headspace ^(c)	Mass spec.	0.30	<1 hour
On-Site	502.2 ^(d)	PID/ELCD ^(e)	0.50	10-14 days
Off-Site	8010/8020 ^(d)	PID/ELCD	0.07	23-27 days

(a) Method detection limit. Note: Method detection limits are compound dependent; values in the table are only approximate.

(b) Values in the table are the actual field-test hold times, not the recommended maximum hold times.

(c) On-site developed method in which 25 mL of the sample is heated inside a 40-mL sample vial at 80°C for 1 hour, and a direct injection of the vial's headspace is made into a gas chromatograph/mass spectrometer operating in selected ion monitoring mode.

(d) U.S. Environmental Protection Agency (EPA). 1983. *Methods for Chemical Analysis of Water and Wastes*, EPA/600/4-79/020, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

(e) Photoionization detector (PID) and electrolytic conductivity detector (ELCD), respectively.

(f) U.S. Environmental Protection Agency (EPA). 1986. *USEPA Methods for Evaluating Solid Waste: Physical/Chemical Methods*, SW-846, 3rd ed. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

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Figure 3.2. Gas Chromatograph/Mass Spectrometer in Field

Table 3.3. Comparison of the Field and On-Site Methods' Accuracy and Precision

Compound	Expected Conc. ($\mu\text{g/L}$)	Field			On-Site		
		Average	% Bias	RSD ^(a)	Average	% Bias	RSD ^(a)
Benzene	21.6	18.3	-15.3	2.2	21.1	-2.3	0.9
Bromodichloromethane	37.2	39.5	6.2	3.3	37.2	0.0	3.0
Chloroform	26.4	25.0	-5.3	2.8	29.0	9.8	3.8

(a) Relative standard deviation.

3.3 Waste Stream Dynamics Tests

Waste stream dynamics were tested by making controlled releases of a tracer material (i.e., a fluorescent dye) into facility waste streams and monitoring the tracer concentrations near the point of release and at end-of-pipe.

Two fluorescent dyes, acid red #52 and rhodamine WT, were used as tracers in the tests. Acid red #52 was used in 1994, while rhodamine WT was used in 1995. In each test, the dye's concentration was monitored using fluorometers. Continuous sampling and real-time data acquisition were achieved by pumping a portion of the waste stream through a flow cell mounted inside the fluorometers. The temperature of the waste stream was also continuously measured for later correction of the fluorescence measurements.

3.3.1 Tests Performed

Buildings were selected for testing based on their proximity to end-of-pipe, their average waste stream flow rate, and the amount of routine-monitoring data from each facility that was available for comparative purposes. Initial tests at 331 and 3720 Buildings in February 1994, 1) generated information to refine the test design, 2) evaluated field logistics, and 3) developed the dye measurement system.

Eighteen tests were performed during 1994 at 331 and 3720 Buildings, and 17 tests were conducted during 1995 at 320, 324, and 3720 Buildings. Table 3.4 lists the test dates and the number and types of releases made at each facility. Several of the releases were not useful for quantitative dilution estimates, because the dye concentration at either the facility or at end-of-pipe was too high for the limited dynamic range of the fluorometer. However, the off-scale data were useful for determining transit and clearance times.

Two special tests were conducted during the summer of 1995 at 3720 Building. The first test involved a dye release into the basement sump located in room 6. Liquid effluent from four basement laboratories flows into this sump, which is partially emptied approximately once every hour. Due to the way liquid is removed from the sump (i.e., building source water is rapidly pumped through a venturi to create a suction effect that draws liquid out), the flow rate of the building's waste stream increases from approximately 1 to 70 gal/min as the sump's fluid level is lowered. Thus, the purpose of the test was to evaluate the stream dynamics in the presence of sump activity and under these high flow-rate conditions. In the second test, a solution containing rhodamine WT and hexone (i.e., methyl isobutyl ketone) was released into the process sewer via an upstairs laboratory sink. Following the release, the dye's concentration was monitored in the normal manner, and 40-mL VOC grab samples were sequentially collected at 1- to 3-minute intervals while the dye was being detected. Approximately 25 samples were collected in this manner at the facility and at end-of-pipe. Samples were stored in ice chests, transported to the on-site laboratory, and analyzed within 48 hours for hexone. The results of the test made it possible to compare the behavior of the dye with that of a real waste stream contaminant.

Table 3.4. Test Dates and Number of Dye Releases

Building	Date of and Number of Dye Releases														
	1994						1995								
	7/1	7/7	7/8	7/11	7/14	7/21	7/7	7/11	7/12	7/13	7/24	7/25	8/3	8/4	8/8
320	--	--	--	--	--	--	--	--	--	1 ^(b)	1 1 ^(b)	1 ^(b)	--	--	--
324	--	--	--	--	--	--	--	--	--	--	--	--	2	3	--
331	--	1 ^(a)	--	1 ^(a)	2	2 ^(b)	--	--	--	--	--	--	--	--	--
3720	1 ^(a,b) 2 ^(a)	1 1 ^(a) 1 ^(b)	2 ^(a)	1 3 ^(b)	--	--	2 ^(a)	4	1 ^(c)	--	--	--	--	--	1 ^(d)

(a) Detection at end-of-pipe only.
 (b) Off-scale measurement(s); data not useful for dilution estimates.
 (c) Release was made into the basement sump located in room 6.
 (d) Special test involving the release of a rhodamine WT and hexone solution.

3.3.2 Time Measurements and Calculation of Dilution Factors

Three types of time measurements were collected in each waste stream dynamics test: arrival time, transit time, and clearance time (Figure 3.3). Arrival time is the time at which a contaminant is first detected at end-of-pipe. Transit time is the time required for the maximum concentration to reach end-of-pipe. Clearance time is the time required for a released constituent to completely flow past a specific location. For a release that results in a single peak (i.e., no sump activity), the clearance time is simply the peak width. Where intercepting sumps are present, the clearance time spans from the beginning of the first peak to the tail of the last peak. Clearance times were determined at the facility sampling points and at end-of-pipe. Dilution factors were determined by dividing the maximum concentration of dye determined at end-of-pipe (i.e., based on peak height) by the maximum concentration of dye determined at the facility release point (i.e., based on peak height).

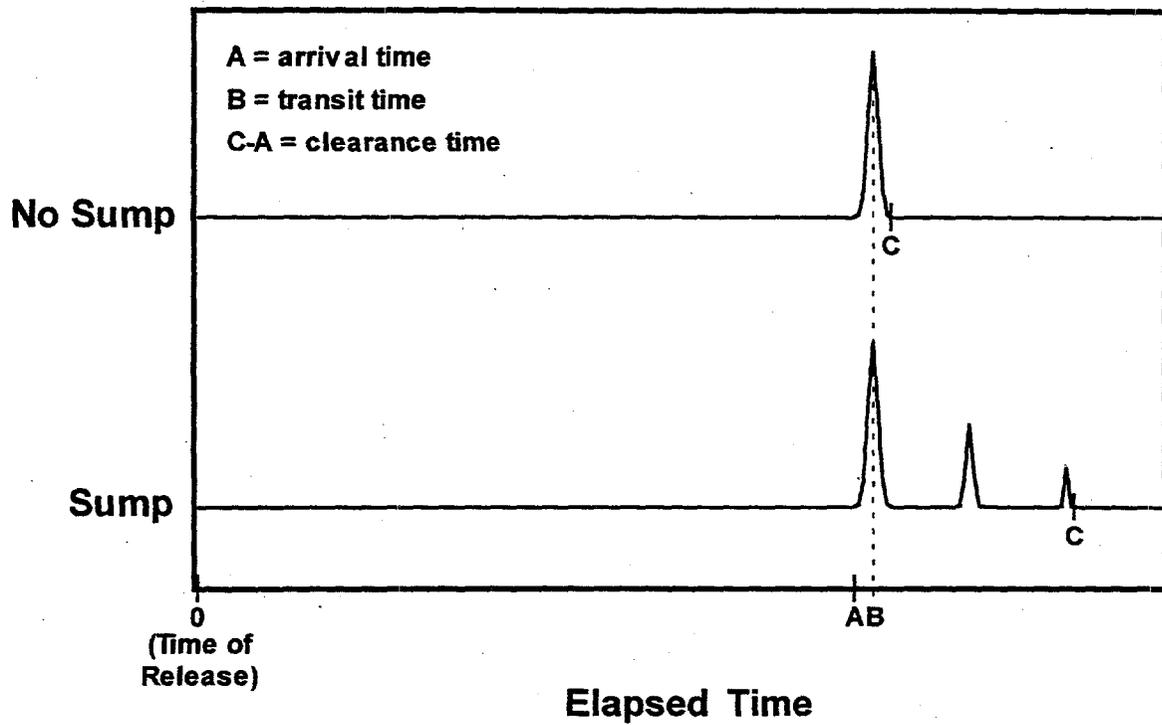


Figure 3.3. Graphical Depiction of Time Measurement Definitions

4.0 Results and Discussion

4.1 331 Building Operation Staff Interviews

Cage and glass washing were found to be frequent, although not regularly scheduled, activities that are conducted to support life sciences research. Detergents, acids, and bases are used in the wash cycles, and phosphate and nitrate are likely to be present in the discharge streams. In addition, a spray wash system, which is used to control building humidity, may discharge potassium hydroxide and sodium molybdate to the process sewer.

4.2 Continuous Monitoring

The continuous-monitoring profiles of pH, conductivity, and flow of the liquid effluent from the 331 Building from February 11 through February 24, 1995, are in Appendix A; profiles from July 11 through July 21, 1995 are in Appendix B; and data from August 23 through September 8, 1995 (excluding August 25 through 30, 1995) are in Appendix C. Analysis of these profiles led to the following findings:

- With three exceptions (February 18, July 16, and September 3, 1995), no significant changes in pH and/or conductivity were observed on Saturdays or Sundays.
- Small, cyclical fluctuations in conductivity and pH occurred at approximately 1- to 2-hour intervals on weekdays and weekends during July, August, and September. The reproducibility of the fluctuations suggest they are associated with an automated process, such as activation of a sump pump or a cooling water flush.
- On weekdays, all events occurred during regular work hours (6:00 a.m. to 6:00 p.m.).
- In most cases, the greatest event activity occurred on Wednesdays, followed by Mondays with lesser activity on Tuesdays, Thursdays, and Fridays.
- In the majority of cases, large changes in conductivity were associated with increases or decreases in pH.
- Significant changes in pH and/or conductivity were not always accompanied by increased stream flow. In some instances, changes in waste stream pH to below 1.0 were associated with a significant lowering of stream flow.
- Conductivity levels ranged from a low of 120 μS on the weekends to 1,800 μS during regular work hours.
- The waste stream pH was 7.5 to 7.6 on weekends and ranged from below 1.0 to 11.0 during regular work hours.

- Flow rates during events varied from weekend levels of 3 to 12 gal/min (11.4 to 45.4 L/min) to as high as 50 gal/min (189.3 L/min).
- Duration of individual events ranged from approximately 5 minutes up to 50 minutes.
- Two patterns of events appeared to occur on a frequent basis.

Pattern 1 (Figure 4.1a, 13:10 to 14:20 hours) was quite pronounced and consisted of a strong conductivity peak immediately followed by one or two conductivity peaks of similar or smaller size. The pH associated with this pattern fluctuated between 3 and 12. The duration of each event in the pattern was approximately 20 to 30 minutes and the pattern would repeat itself anywhere from two to four times at approximately 20-minute intervals. This pattern may be caused by cage or glass washing processes in the building. The large fluctuation in pH may be attributed to insufficient neutralization of highly caustic or acidic chemicals used in these processes. The multiple, diminishing event peaks associated with this pattern are consistent with a wash cycle followed by a rinse cycle.

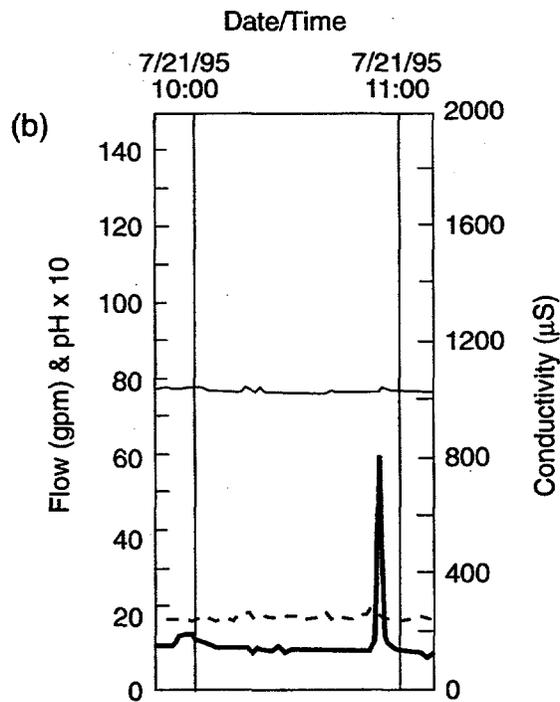
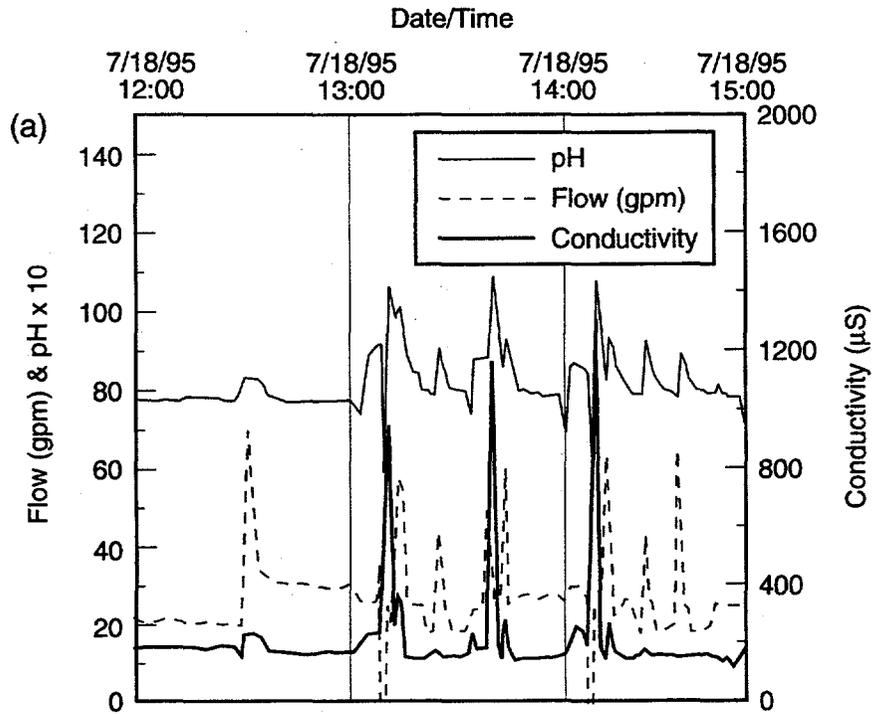
Pattern 2 (Figure 4.1b) consisted of an event of low to moderate conductivity and a pH that deviated only slightly from the annual average. The duration of the event lasted approximately 5 minutes. This type of pattern may be a result of ongoing research activities within the 331 Building.

4.3 Event-Triggered Sampling and Qualitative Chemical Analysis

Figures 4.2a, 4.2b, 4.3a, and 4.3b provide a summary of event-triggered sampling points associated with event patterns and the elevated and high levels of anions and metals detected in the analysis of these samples. Elevated levels were defined as contaminant levels that exceeded two times the CY 1994 and 1995 average of routine-monitoring data. High levels were defined as contaminant measurements that exceeded two times the CY 1994 and 1995 maximum observed level for routine-monitoring data. Our ability to adequately set event-triggering parameters can be seen in the sampling of event patterns. In some instances, the sampler was triggered on the up side of a peak, maximizing the likelihood that the sample would contain the maximum concentration of contaminants associated with that peak (event). In other instances, the sampler triggered on the down side of a peak, significantly reducing the representativeness of the collected sample in relation to the event.

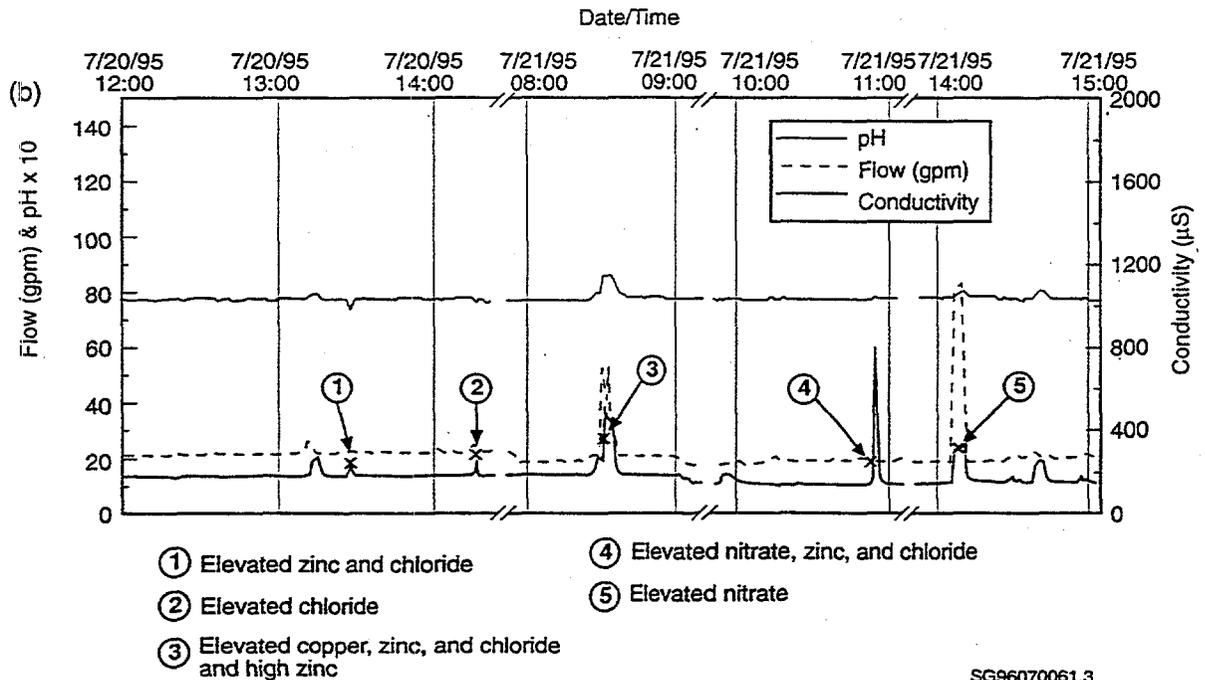
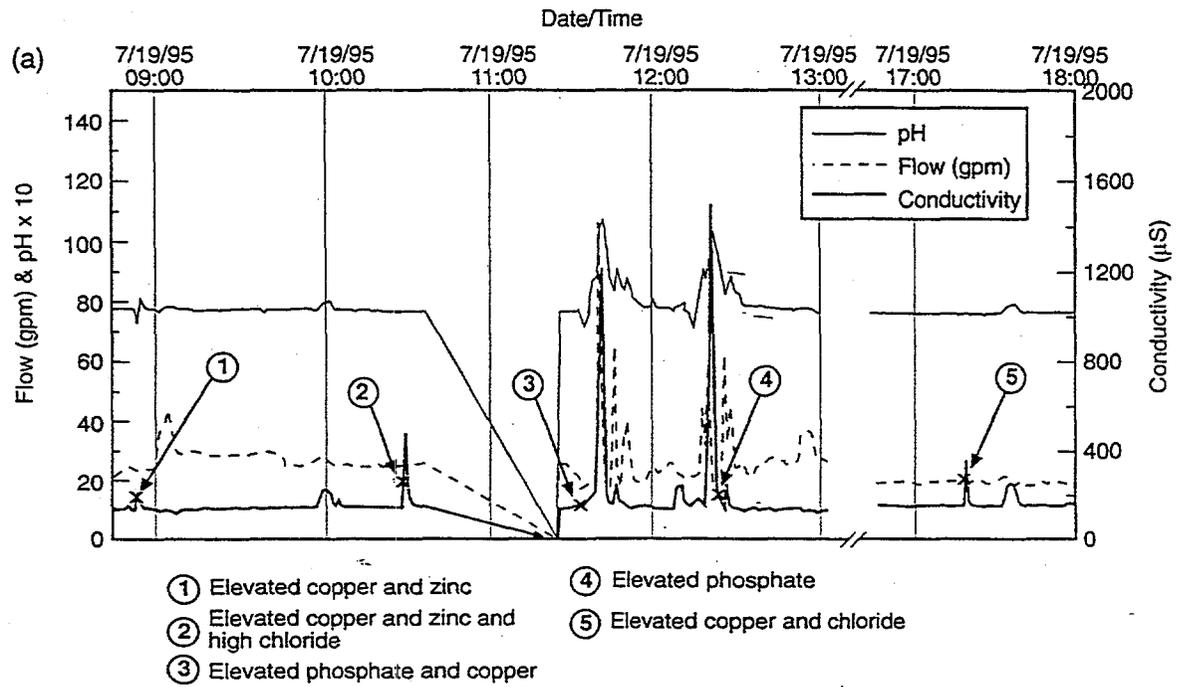
Elevated or high nitrate and phosphate concentrations were commonly found associated with Pattern 1. This appears to be consistent with the chemistry of cage or glass washing activities as indicated from building operations staff interviews (Section 4.1). Elevated or high levels of fluoride were also found associated with this type of pattern.

Pattern 2 tended to have some combination of elevated or high levels of copper, zinc, chloride, and sulfate, suggesting possible discharges of inorganic salt solutions to the process sewer. These discharges may be associated with ongoing research activities in the building.



SG96070061.2

Figure 4.1. Frequently Observed Event Patterns: Pattern 1 (a) and Pattern 2 (b)



SG96070061.3

Figure 4.2. Qualitative Chemistry of Events (7-19-95 through 7-21-95)

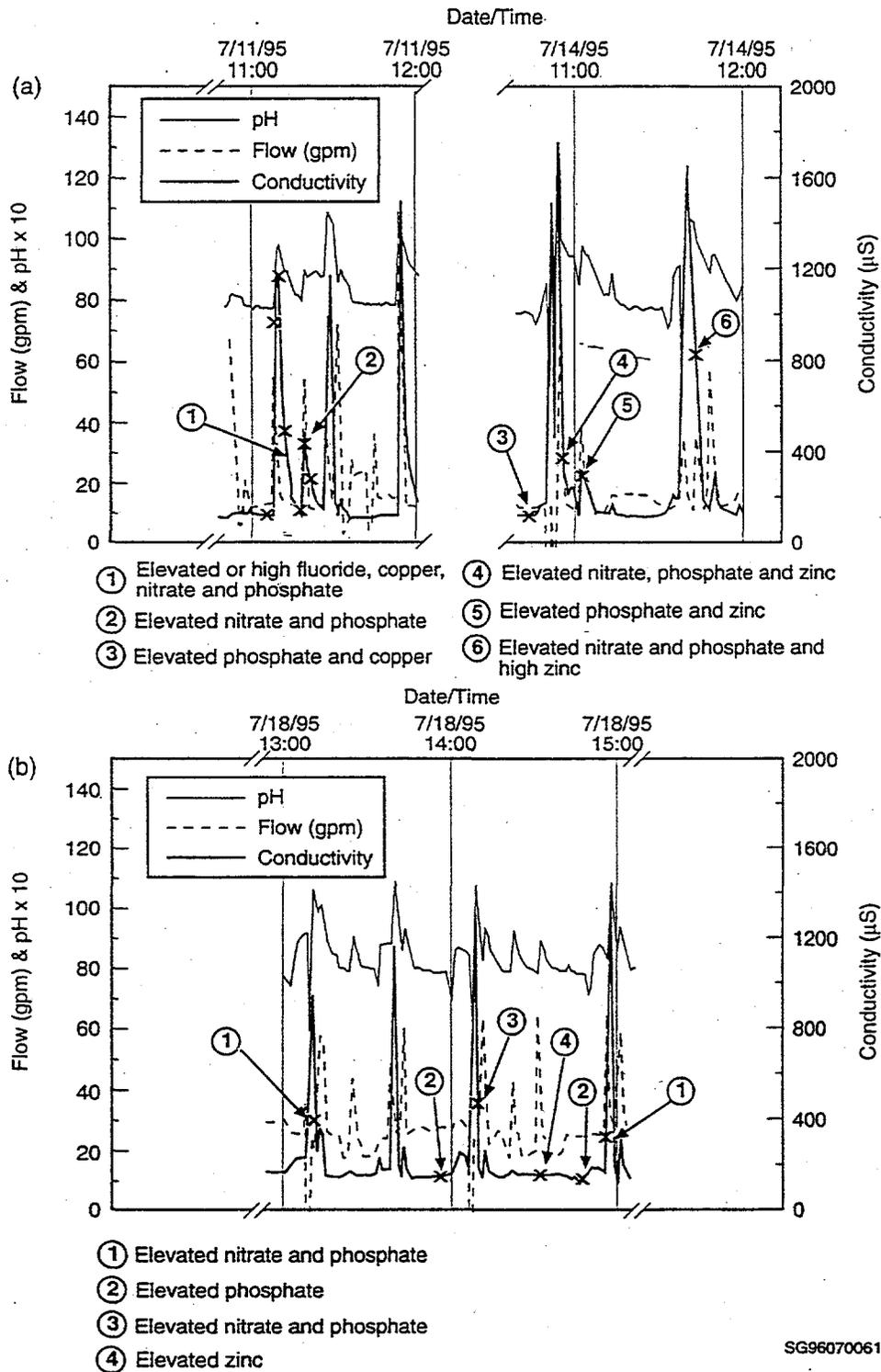


Figure 4.3. Qualitative Chemistry of Events (7-11-95 through 7-18-95)

4.3.1 Analysis of Event-Triggered Samples: Anions and Metals

Tables 4.1 and 4.2 summarize data on general parameters and concentrations (elevated and high level) of selected anions and metals in samples analyzed from event-triggered sampling in July and August to September 1995. Complete data sets for campaigns 1 and 2 event-triggered sampling and analysis can be found in Appendixes D and E.

The pH of event-triggered samples collected from the 331 Building liquid waste stream during the July and August to September 1995 campaigns ranged from a low of 7.16 to a high of 10.50. Conductivity ranged from a low of 126.8 μS to a high of 1,182.0 μS . These values are in contrast to pH values ranging from 3.34 to 8.84 and a maximum conductivity reading of 920 μS observed during CY 1994 and CY 1995 routine monitoring of the 331 Building liquid waste stream. Average pH and conductivity values of the waste stream for CY 1994 and CY 1995 were 7.47 and 241.0 μS , respectively.

A number of the events were found to be associated with elevated and/or high levels of selected contaminants. Sample 7 from August 23, 1995, contained the highest levels of phosphate (809 ppm) and nitrate (212 ppm) observed in both campaigns. Elevated and high levels of sodium and potassium were often observed in the presence of high phosphate. The fluoride concentration, 4.68 $\mu\text{g}/\text{mL}$, was also one of the highest. The high nitrate concentration exceeded the EPA drinking water standard (10 ppm) by a factor of 80, and fluoride exceeded the drinking water standard by 20%. Significantly high levels of these contaminants were also observed in event samples collected on July 11, along with the highest conductivity levels observed during the field test (1,182 and 1,118 μS).

Several events (July 19, samples 15 and 16, and July 21, sample 8) showed concurrent elevated or high levels of copper, zinc, chloride, and sulfate. In these situations, pH was near the CY 1994 and CY 1995 average. These data suggest metal salts (e.g., copper or zinc sulfates or chlorides) may have been discharged as a part of ongoing facility research activities. In a couple of cases, copper exceeded the TEDF WAC by as much as a factor of 8 (sample 16 on July 19, 1995). In one sample, zinc also exceeded the TEDF WAC by a factor of 8 (sample 8, July 21, 1995). Aluminum, chromium, and magnesium exceeded TEDF WAC on one or two occasions during the August to September campaign.

Some events (not shown) occurred on a fairly regular basis (including off hours and weekends) and showed slightly elevated pH and conductivity (e.g., samples 1, 2, 17, and 19 on August 23, 1995) and no elevated or high levels of inorganic contaminants of interest.

4.3.2 Event-Triggered Analysis: Volatile Organic Compounds

Table 4.3 summarizes the analysis of selected campaign 2 event-triggered samples for VOCs. Two VOCs that are commonly found associated with water treatment (i.e., chloroform and bromodichloromethane) were most often detected in these samples. The average concentration of chloroform was $23 \pm 12 \mu\text{g}/\text{L}$, which was almost a factor of 2 higher than the CY 1994 and CY 1995 average ($12 \pm 7 \mu\text{g}/\text{L}$) for 331 Building effluent. The average concentration of bromodichloromethane for event samples was $3.5 \pm 3 \mu\text{g}/\text{L}$ versus $2.5 \pm 2.5 \mu\text{g}/\text{L}$ for CY 1994 and CY 1995 routine-monitoring samples. These slightly elevated levels do not suggest that large releases of these chemicals occurred during the events that were monitored. Benzene, tetrahydrofuran, and several chlorinated solvents were sporadically detected at concentration levels in the range of 0.5 to 23 $\mu\text{g}/\text{L}$.

Table 4.1. 331 Building Event-Triggered Sample Data: July 1995^(a) (Campaign 1)

Date	Day	Sample Number	Pattern Print ^(b)	Time	pH	Cond (μS)	Anion/Metal (ppm)							
							F	Cl	NO ₃	PO ₄	SO ₄	NO ₂	Cu	Zn
7/11/95	Tues	14	1	11:08	7.83	134.2	2.7		108.9	369.7				
7/11/95	Tues	15	1	11:09	9.75	1118	2.96		138.7	482.7				
7/11/95	Tues	16	1	11:10	9.9	1182	2		105.7	366.2				
7/11/95	Tues	17	1	11:12	9.08	466.1	1.79		53.3	166.3				
7/11/95	Tues	18	1	11:17	8.27	168.5				19.9				
7/11/95	Tues	19	1	11:19	9.05	472.2			24.1	60.9				
7/11/95	Tues	20	1	11:20	8.79	277.1			27.6	71.6				
7/13/95	Thurs	3	2	14:23	8.41	287.5								
7/13/95	Thurs	4	2	14:35	6.93	174.8	2.39							0.23
7/13/95	Thurs	5	2	15:34	8.42	287.7								
7/14/95	Fri	1	1	10:44	7.46	131.9				26.9			0.138	
7/14/95	Fri	2	1	10:54	9.91	384.3			17.3	59.2				0.22
7/14/95	Fri	3	1	11:42	10.5	847.4			12.1	41.4				0.48
7/14/95	Fri	4	1	11:04	9.31	241.2				18.5				0.22
7/18/95	Tues	3	1	13:11	10.13	395			21.5	37.5				
7/18/95	Tues	7	1	13:58	7.46	151.4								
7/18/95	Tues	8	1	14:08	10.19	445.5			23.2	74.7				
7/18/95	Tues	10	1	14:32	8.94	162.3								0.18
7/18/95	Tues	11	1	14:48	7.45	148.3								
7/18/95	Tues	12	1	14:58	9.76	312.3			15	28.2				
7/19/95	Wed	15	2	8:52	7.41	189.4							0.138	0.15
7/19/95	Wed	16	2	10:28	7.77	272		63.4					0.664	0.21
7/19/95	Wed	1	1	11:34	7.24	166.6				16.5				
7/19/95	Wed	4	1	12:24	9.16	204.3				16.8				
7/19/95	Wed	5	2	17:19	7.68	283.3		57					0.325	
7/20/95	Thurs	6	2	13:27	7.52	219.3		36.9						0.12
7/20/95	Thurs	7	2	14:15	7.6	286.3		59.1						
7/21/95	Fri	8	2	8:29	8.05	293.4	1.72	25.8			72.3		0.152	1.6
7/21/95	Fri	9	2	10:53	7.68	265.9		69.6	30.4					0.24
7/21/95	Fri	10	2	14:09	7.9	297.5			15.6					
94/95 Avg ^(c)					7.47	241	0.64	10.2	5.4	6.8	19.2	0.17	0.046	0.066
94/95 Max ^(d)					3.30/ 8.84	920	1.1	167	33	81.7	47.9	0.2	0.93	0.23

Table 4.1. (contd)

Date	Day	Sample Number	Pattern Print ^(b)	Time	pH	Cond (μ S)	Anion/Metal (ppm)							
							F	Cl	NO ₃	PO ₄	SO ₄	NO ₂	Cu	Zn
MCL ^(e)							4		10			1	1.3	
WAC ^(f)												0.4	0.08	0.21

(a) Unbolded contaminant measurements exceed 2 times the CY 1994 and CY 1995 average of routine-monitoring data for the 331 Building and are classified as elevated levels. Bolded contaminant measurements exceed 2 times the CY 1994 and CY 1995 maximum observed for routine-monitoring data and are classified as high levels.
 (b) Pattern to which the event peak has been assigned (see Section 4.2).
 (c) Average observed from grab and 24-hour composite samples collected from 331 Building process sewer during Pacific Northwest National Laboratory routine liquid effluent monitoring.
 (d) Maximum observed (for pH the high and low observed) from grab and 24-hour composite samples collected from 331 Building process sewer during Pacific Northwest National Laboratory routine liquid effluent monitoring.
 (e) U.S. Environmental Protection Agency maximum contaminant levels for drinking water (EPA 1994).
 (f) Treated Effluent Disposal Facility waste acceptance criteria.

Event samples collected on July 20 during campaign 1 contained high (exceeding 2 times the CY 1994 and CY 1995 maximum) levels of acetone and isopropyl alcohol. High levels of acetone were also detected in samples collected on July 21 (Table 4.3). Acetone concentrations in event-triggered samples from both days ranged from 70 to 430 μ g/L. Acetone concentrations in CY 1994 and CY 1995 routine monitoring of 331 Building effluent ranged from 5.6 to 1,800 μ g/L. During the two July 20 events, the range in isopropyl alcohol concentration was 580 to 901 μ g/L. Isopropyl alcohol was only detected in one CY 1994 and CY 1995 routine-monitoring sample from the 331 Building; the concentration was 19 μ g/L. Not surprisingly, the July 20 events containing the high levels of acetone and isopropyl alcohol were associated with very low conductivity and pH responses. See Figure 4.2b.

4.3.3 Impact of Events on End-of-Pipe Concentrations

Maximum concentrations observed in event samples of selected regulated contaminants (fluoride, nitrate, copper, and zinc) were used to estimate concentrations at end-of-pipe based upon an average dilution factor of 524 for the 331 Building determined during FY 1994 stream dynamics tests. The results of those estimations are summarized in Table 4.4. In all cases, contributions from these 331 Building events to total end-of-pipe concentrations were estimated to be below TEDF WAC or EPA MCLs.

Table 4.4 also summarizes the concentration of fluoride, nitrate, copper, and zinc observed in routine-monitoring samples collected from end-of-pipe during CY 1994 and CY 1995. In all cases, average concentrations of these contaminants were below TEDF WAC and EPA MCL. With one exception (i.e., nitrate), maximum end-of-pipe concentrations also did not exceed TEDF WAC or EPA MCL. Concentrations as high as 110 mg/L of nitrate were observed at end-of-pipe during CY 1994 and CY 1995. These levels likely resulted from releases containing contaminant levels significantly above those observed in the field test (i.e., from concentrated releases from one or more 300 Area facilities).

Table 4.3. Concentration ($\mu\text{g/L}$) of Volatile Organic Compounds in 331 Building Event Samples: July 1995 (Campaign 1)

Compound	Sample Collection Date/Sample Number																											
	07/11/95												07/18/95												07/20/95		07/21/95	
	#14	#15	#16	#17	#18	#19	#20	#3	#7	#8	#10	#11	#12	#15	#16	#1	#4	#5	#6	#7	#8	#9	#10					
Isopropyl Alcohol																			580	901								
Acetone																			70	128	380	430	100					
Methylene Chloride								5.1																				
cis-1,2-DCE ^(a)	23																											
Chloroform		13	17	18	24	9.5	13	38	29	46	23	33	45	16	26	28	18	20	14	20	9.9	43	6.5					
Tetrahydrofuran	10											1.0																
1,1,1-TCA ^(b)	15						0.7					1.3																
Carbon Tetrachloride	3.6															1.0		0.7		1.2		0.6	0.5					
1,2-Dichloroethane	3.0																											
Benzene																	1.1		0.8			2.0						
Trichloroethene																												
Bromodichloromethane				0.6	2.0			8.1	5.1	7.4	1.7	5.4	8.3		2.6	4.0	0.6	0.7	0.8	1.5		2.9						
Tetrachloroethene									1.1			0.6																

(a) cis-1,2-Dichloroethylene.

(b) 1,1,1-Trichloroethane.

Table 4.4. 331 Building Event and End-of-Pipe Concentrations (mg/L) and Regulatory Interrelationships

Contaminant	Maximum Event Concentration Observed	Estimated Concentration at End-of-Pipe ^(a)	CY 1994-1995 Average End-of-Pipe Concentration	CY 1994-1995 End-of-Pipe Concentration Range	Treated Effluent Disposal Facility Waste Acceptance Criteria (mg/L)	U.S. Environmental Protection Agency Maximum Contaminant Level (mg/L)
Fluoride	7.78	0.015	0.55	0.20-0.94	--	4
Nitrate	212	0.4	6.1	0.2-110	--	10
Copper	0.66	0.001	0.018	0.008-0.049	0.08	1.3
Zinc	1.6	0.003	0.041	0.019-0.110	0.21	

(a) An average dilution factor of 524 was used based upon results of FY 1994 stream dynamics tests (see Section 4.5.4 and Table 4.11).

4.4 Volatile Organic Compound Hold-Time Study

The field- and laboratory-measured concentrations of VOCs in each of the grab samples collected during the VOC hold-time study field test are graphed in Appendix F. The data were evaluated from three perspectives: 1) VOCs identified and frequency of detection, 2) VOC concentrations determined and data significance, and 3) comparison of VOC hold-time study data with CY 1994 and CY 1995 VOC routine-monitoring data.

4.4.1 Volatile Organic Compounds Identified and Frequency of Detection

Sixteen VOCs were detected with varying frequencies in samples analyzed in the field and at the two laboratories (see Figure 4.4). The number of analytes detected at each location varied significantly: 14 were found in field-analyzed samples, 5 were detected in on-site analyzed samples, and 3 were measured in samples analyzed off-site. Chloroform was the only compound that was detected in every sample analyzed at all three locations. Nine VOCs (i.e., bromoform, carbon tetrachloride, 1,1-dichloroethane, 1,2-dichloroethane, *trans*-1,2-dichloroethene, ethylbenzene, hexone, toluene, and 1,1,1-trichloroethane) were detected only in field-analyzed samples. False detection of these compounds in the field was possible but unlikely because the concentrations were always at least 2 times greater than the method detection limits (MDLs). Bromoform and hexone were not measured in the off-site method of analysis. However, off-site MDLs for the other seven compounds detected in field-analyzed samples were approximately 4 to 10 times lower than the corresponding field-method MDLs. Thus, failure of the off-site laboratory to detect these analytes cannot be attributed to lower method sensitivity. A more likely explanation for nondetection is that losses occurred during sample transport and storage that resulted in VOC levels in samples falling below off-site MDLs. Acetone and trichloroethene were only detected in samples analyzed by the on-site laboratory. Acetone is not quantitated in the off-site method and has a relatively high MDL in the headspace method. Trichloroethene may have been falsely detected in on-site analyses, because its low concentration (0.6 µg/L) was very near the MDL (0.5 µg/L).

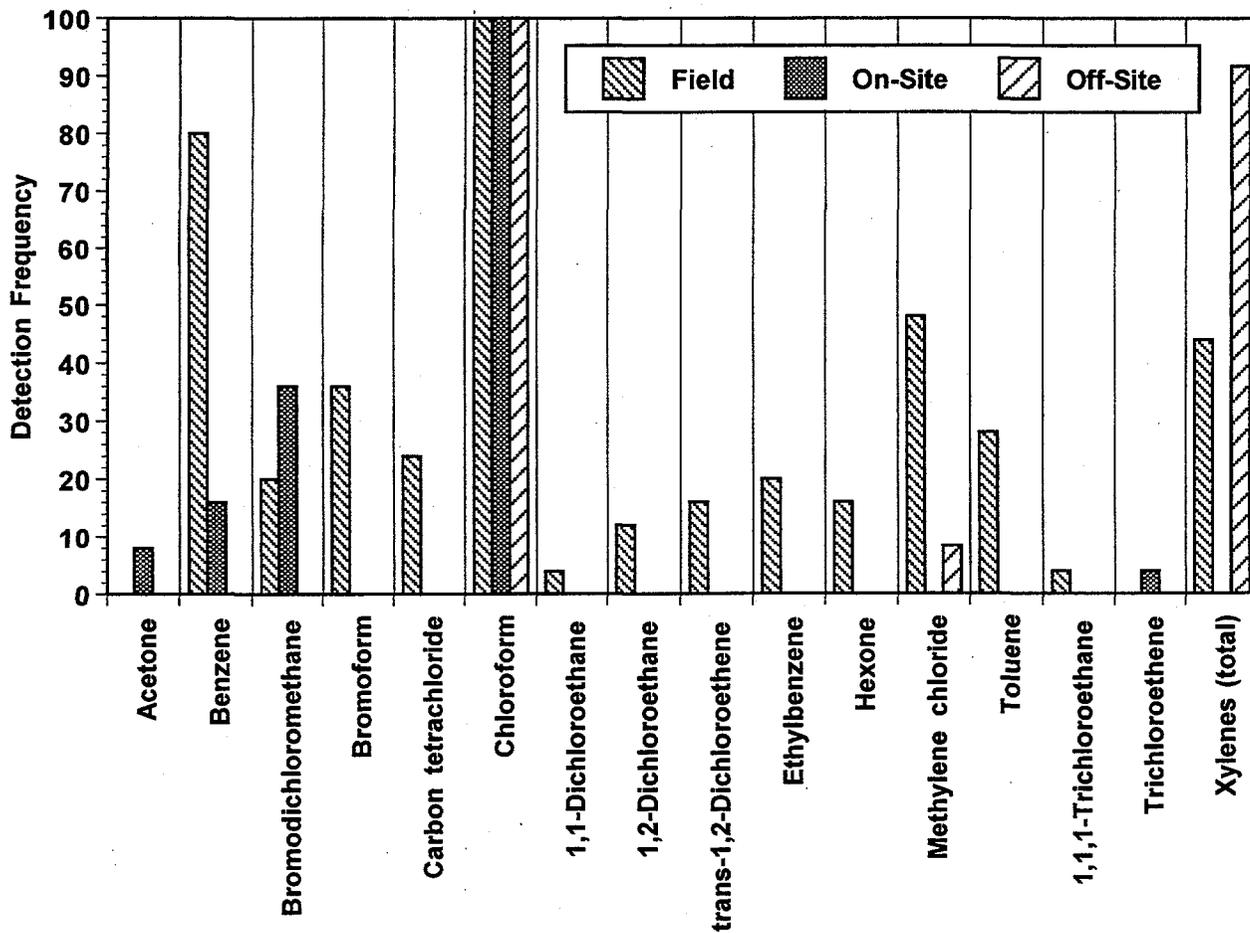


Figure 4.4. Volatile Organic Compound Detection Frequencies

4.4.2 Volatile Organic Compound Concentrations Determined and Data Significance

Figure 4.5 summarizes the average and range of concentrations of VOCs measured in the field and by on-site and off-site laboratories. Chloroform had the highest average concentration in samples analyzed in the field ($30.5 \mu\text{g/L}$) and at the off-site laboratory ($12.9 \mu\text{g/L}$). One sample (sample 31) had a measured chloroform concentration of $138 \mu\text{g/L}$ in the field and $68.3 \mu\text{g/L}$ at the on-site laboratory (Figure 4.6). These unusually high levels suggest that a brief event involving a chloroform release from the 331 Building was occurring when this sample was being collected. This conclusion is supported by the fact that much lower concentrations of chloroform were observed in the samples collected approximately 30 minutes before and after sample 31 (samples 30 and 32 in Figure 4.6). More importantly, the detection of the event was not obviously discernible from the off-site data, because the measured chloroform concentration of $22 \mu\text{g/L}$ was barely distinguishable from background levels.

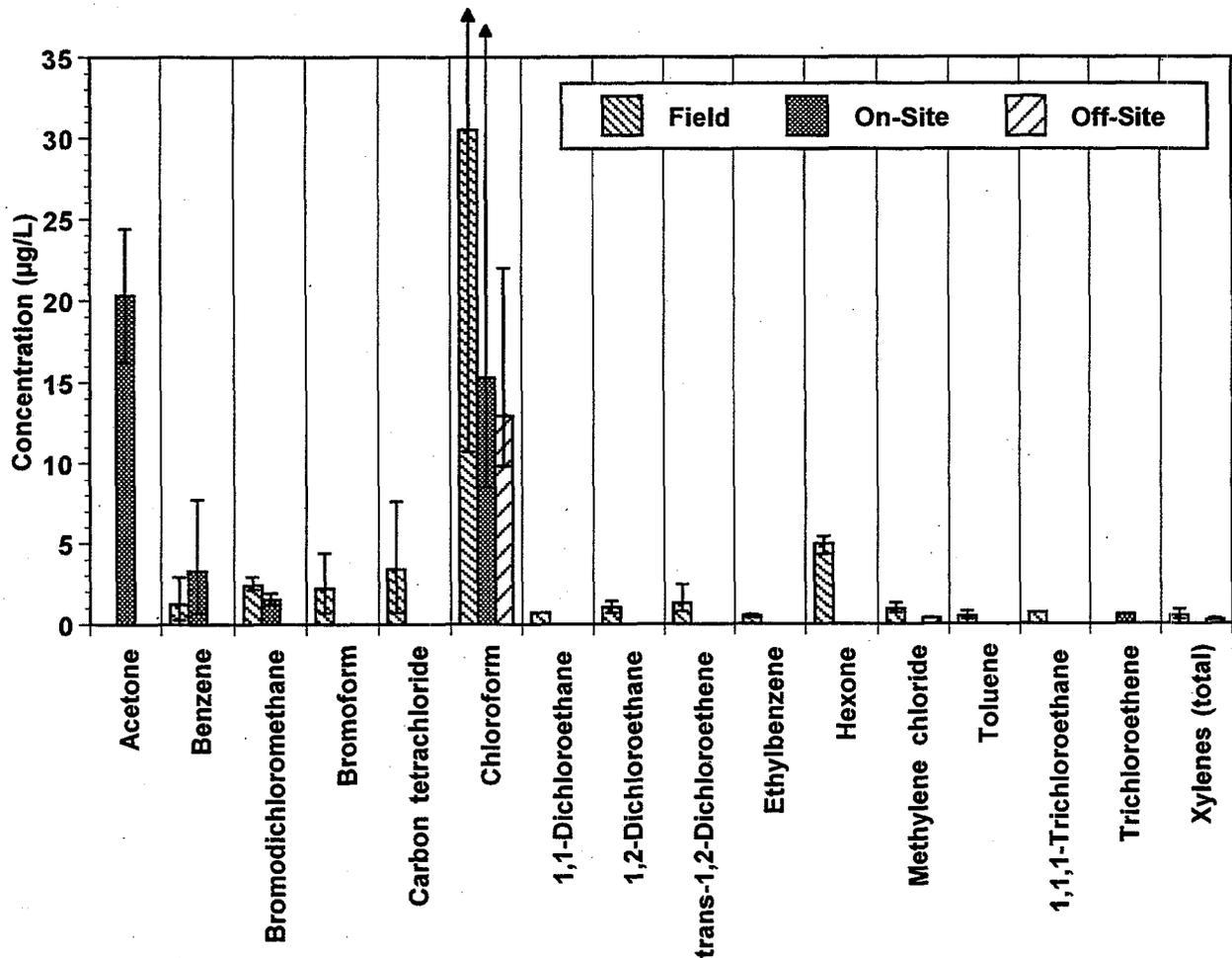


Figure 4.5. Volatile Organic Compound Average Concentrations

Acetone had the highest average concentration (20.3 $\mu\text{g/L}$) of constituents measured in off-site-analyzed samples. Benzene, carbon tetrachloride, and hexone all had at least one in-field or on-site measurement above 5 $\mu\text{g/L}$. Average concentrations of the remaining VOCs were all less than 3 $\mu\text{g/L}$ for all analysis locations (Figure 4.5).

The performances of the in-field, on-site and off-site processes used for VOC sample handling and analysis were compared by calculating the relative percent differences in concentration for each compound that was detected more than once in the same sample by the different processes. Nondetects were not included in the analysis due to the different sensitivities of the analytical methods (see Table 3.2). Table 4.5 summarizes the average relative percent differences for benzene, bromodichloromethane, chloroform, methylene chloride, and xylenes (totals). With the exception of benzene, measured field concentrations were generally 1.5 to 3 times higher than concentrations measured by the on-site and off-site laboratory. However, based on the low relative standard deviations and biases

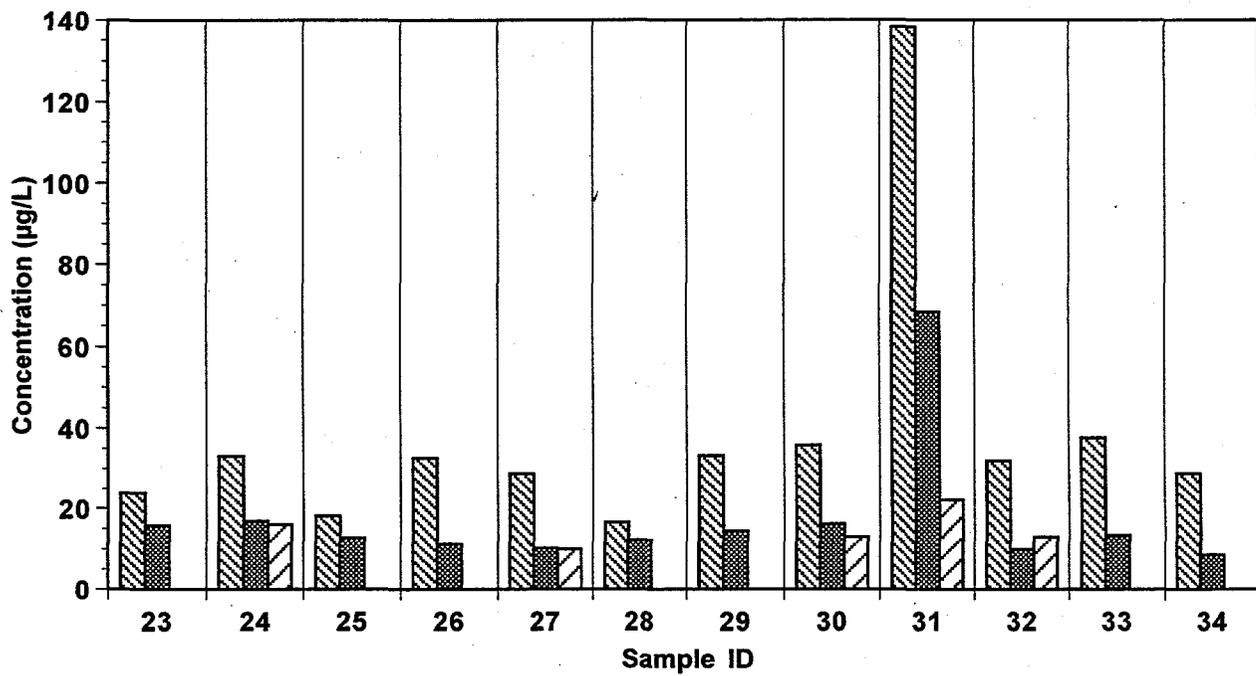
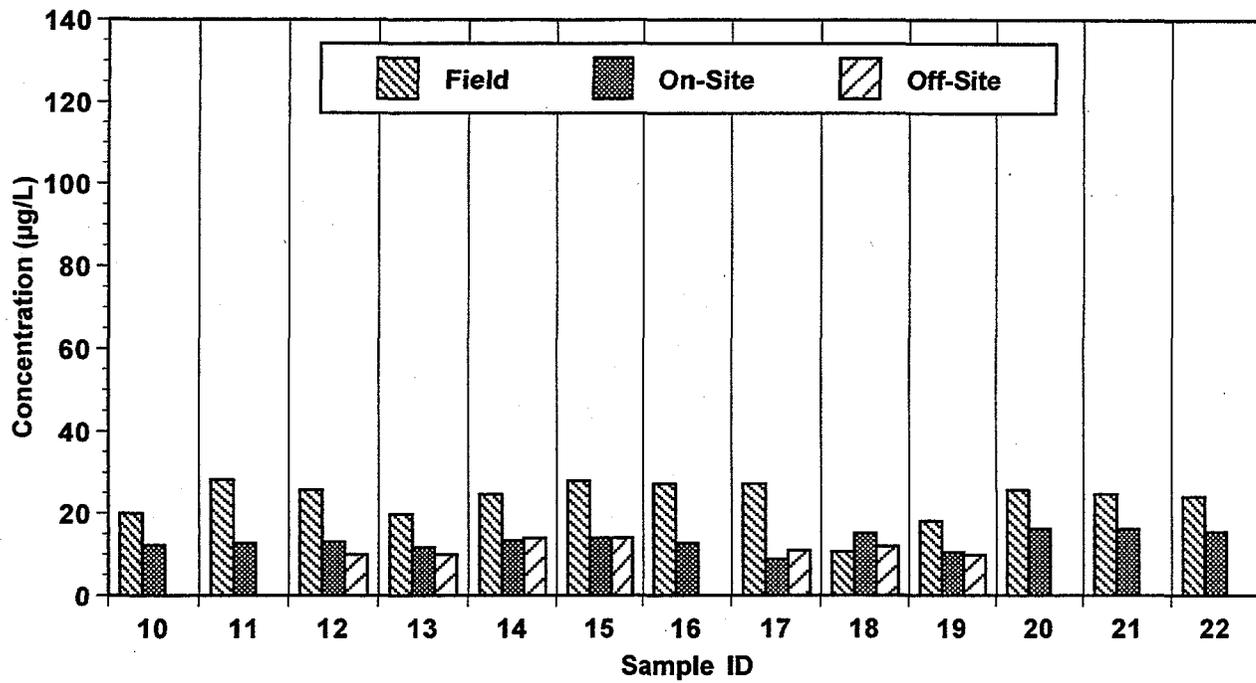


Figure 4.6. Measured Concentrations of Chloroform in Samples from Hold-Time Study

Table 4.5. Average Relative Percent Differences in Volatile Organic Compound Concentration

Analyte	n ^(a)	Field/On-Site	Field/Off-Site		On-Site/Off-Site	
		Average relative percent differences	n ^(a)	Average relative percent differences	n ^(a)	Average relative percent differences
Benzene	4	-59.1	0	--	0	--
Bromodichloromethane	3	46.8	0	--	0	--
Chloroform	25	63.3	12	74.8	12	12.6
Methylene chloride	0	--	1	106	0	--
Xylenes (total)	0	--	4	54.0	0	--

(a) Number of samples in which the analyte was detected by both methods of analysis.

demonstrated for field and on-site methods (Table 3.3), the differences between the field and on-site results in Table 4.5 cannot be attributed to differences in the methods' precision and accuracy.

The most reliable comparisons of results can be made using the chloroform data, because chloroform was the most frequently detected analyte, and the concentrations were well above the MDLs. All of the samples except one (sample 18) had the highest concentrations determined in the field. For the most part, the lowest chloroform concentrations were found in samples analyzed by the off-site laboratory (Figure 4.6). This trend in relative concentrations (i.e., field >> on-site ≥ off-site) is consistent with the number of VOCs detected and the belief that losses occurred during transport and storage of the samples set aside for on-site and off-site analyses. Moreover, the relatively close agreement in data between the on-site and off-site laboratories suggests that most of the losses occurred during the first 10 to 14 days of storage.

4.4.3 Comparison of Volatile Organic Compound Hold-Time Study Data with 331 Building CY 1994 and CY 1995 Routine-Monitoring Data

Sixty-six samples from 331 Building were analyzed for VOCs during CY 1994 and CY 1995 under the routine-monitoring component of the Effluent Management Project. Forty-six of these samples were 24-hour, flow-proportional composites, while the rest were grab samples. Because of the different time periods represented by the samples, the different sampling methods employed, and the dynamic nature of research activities that contribute to the effluent, findings based on the VOC data from the hold-time study and routine-monitoring data should be viewed with caution. Significant findings were as follows.

- Benzene, carbon tetrachloride, 1,1-dichloroethane, 1,2-dichloroethane, *trans*-1,2-dichloroethene, and ethylbenzene were detected in hold-time study field-analyzed samples but were not detected in 1994 or 1995 routine-monitoring samples. In the hold-time study, none of these six compounds were detected in samples analyzed by the off-site laboratory, which performed most of the VOC analyses associated with CY 1994 and CY 1995 routine-monitoring samples (Table 4.6). One of these compounds, 1,2-dichloroethane is on the TEDF WAC. Even in samples analyzed in the field as part of the hold-time study, the concentration of this compound was below the WAC.

Table 4.6. Comparison of Volatile Organic Compound Detection Frequencies in the Hold-Time Study and in CY 1994 and CY 1995 331 Building Routine-Monitoring Samples^(a)

Compound	Hold-Time Study			Routine Monitoring CY 1994 and 1995
	Field	On-Site	Off-Site	
Acetone		2/25		15/66
Benzene	20/25	4/25		
Bromodichloromethane	5/25	9/25		16/34
Bromoform	9/25			1/34
Carbon tetrachloride	6/25			
Chloroform	25/25	25/25	12/12	66/66
1,1-Dichloroethane	1/25			
1,2-Dichloroethane	3/25			
trans-1,2-Dichloroethene	4/25			
Ethylbenzene	5/25			
Hexone	4/25			4/66
Methylene chloride	12/25		1/12	43/66
Toluene	7/25	25/25		4/66
1,1,1-Trichloroethane	1/25			1/66
Trichloroethene		1/25		3/66
Xylenes	11/25		11/12	3/66

(a) Detection frequencies are listed as number of positive detects/number of samples analyzed. Blank entries denote the compound was not detected.

- On the average, on-site and off-site laboratory-measured chloroform concentrations in the hold-time study were approximately half of that detected in field-analyzed samples. The average chloroform concentration for CY 1994 and CY 1995 routine-monitoring data was similar to the on-site and off-site averages found in the hold-time study (Table 4.7). Chloroform exceeded the TEDF WAC of 26 µg/L in 52% (13/25) of the samples analyzed in the field as part of the hold-time study, compared to only 5% (3/66) of the CY 1994 and CY 1995 331 Building routine-monitoring samples analyzed off-site. Excluding sample 31, none of the on-site and off-site laboratory's results exceeded the TEDF WAC in the VOC hold-time study. It is estimated that three on-site and four off-site samples in the select data set of Table 4.7 would have been measured as exceeding TEDF WAC if it were not for the losses occurring during sample transport and storage. These data imply that the TEDF WAC for chloroform was probably exceeded much more frequently during CY 1994 and CY 1995 than the 331 Building routine-monitoring data indicates. For example, based on the 46.9% average VOC loss incurred in off-site analyzed samples as determined in the hold-time study, it is estimated that TEDF WAC exceedances for chloroform may have been as high as 28/66 or 38% higher in the 331 Building routine-monitoring samples than actually observed.

Table 4.7. Comparison of Volatile Organic Compound Hold-Time Study Chloroform Concentrations

Sample Number	Date	Time	Chloroform Concentration ($\mu\text{g/L}$) and Percentages ^(a)				
			In-Field	On-Site	On-Site as % of In-Field	Off-Site	Off-Site as % of In-Field
10	9/7/95	11:44	19.9	12.2	61.3	--	--
11	9/7/95	12:18	28.3	12.7	44.9	--	--
12	9/7/95	12:55	25.7	13.1	51.0	10.0	38.9
13	9/7/95	13:24	19.8	11.7	59.1	10.0	50.5
14	9/7/95	14:02	24.6	13.3	54.1	14.0	56.9
15	9/7/95	14:34	28.0 ^(c)	14.0 ^(d)	50.0	14.0 ^(d)	50.0
16	9/7/95	15:14	27.3 ^(c)	12.7	46.5	--	--
17	9/8/95	10:27	27.3	8.8	32.2	11.0	40.3
18	9/8/95	11:03	10.7	15.2	142.1 ^(e)	12.0	112.2 ^(e)
19	9/8/95	11:52	18.1	10.5	58.0	9.8	54.1
20	9/8/95	12:21	25.7	16.3	63.4	--	--
21	9/8/95	12:49	24.7	16.2	65.6	--	--
22	9/8/95	13:52	24.0	15.5	64.6	--	--
23	9/8/95	14:34	23.9	15.7	65.7	--	--
24	9/8/95	15:01	33.1 ^(c)	16.9 ^(d)	51.1	16.0 ^(d)	48.3
25	9/11/95	09:45	18.1	12.8	70.7	--	--
26	9/11/95	10:38	32.6	11.3	34.7	--	--
27	9/11/95	11:09	28.7 ^(c)	10.3	35.9	10.0	34.8
28	9/11/95	11:40	16.6	12.2	73.5	--	--
29	9/11/95	12:12	33.2	14.4	43.4	--	--
30	9/11/95	13:23	35.8 ^(c)	16.1 ^(d)	45.0	13.0 ^(d)	36.3
31 ^(b)	9/11/95	13:55	138.3 ^(c)	68.3		22.0	
32	9/11/95	14:26	31.9 ^(c)	9.9	31.0	13.0 ^(d)	40.8
33	9/11/95	14:57	37.5	13.4	35.7	--	--
34	9/11/95	15:40	28.7	8.5	29.6	--	--
$\bar{x} \pm \sigma$, all data ^(f)			26.0 \pm 6.5	13.1 \pm 2.4	50.7	--	--
$\bar{x} \pm \sigma$, partial data set ^(g)			25.8 \pm 7.3	12.7 \pm 2.7	49.2	12.1 \pm 2.1	46.9

(a) The average chloroform concentration measured in CY 1994 and CY 1995 routine-monitoring samples from 331 Building by the off-site laboratory was 12.4 \pm 6.4 $\mu\text{g/L}$.
 (b) Sample 31 was excluded from the calculation of average concentrations.
 (c) Samples where the chloroform concentration exceeded the TEDF WAC and where on-site and off-site laboratory data was available for comparative purposes.
 (d) Based on the average on-site and off-site measurements as a percent of in-field measurements, samples where chloroform concentrations likely exceeded the TEDF WAC but were not indicated as such in on-site and off-site sample analyses due to losses incurred during sample storage and transport.
 (e) Sample 18 was excluded from the calculation of average percentages based on the results of the Q test.
 (f) Average \pm standard deviation or average percentage; calculated using all in-field and on-site sample data.
 (g) Calculations for this row included only those samples that were analyzed at all three locations.

4.4.4 Influence of Hold-Time Bias on Volatile Organic Compound Exceedances at End-of-Pipe

The effect of low VOC bias on routine-monitoring data exceedances of TEDF WAC at end-of-pipe was assessed for eight compounds. Table 4.8 summarizes the results of this assessment. For five of the constituents (methylene chloride, tetrachloroethene, toluene, 1,1,1-trichloroethane, and trichloroethylene), TEDF WAC would not have been exceeded for reported concentrations taking into account VOC hold-time bias (i.e., maximum concentration in range multiplied by maximum VOC hold-time bias is less than TEDF WAC). For seven of the constituents (excluding chloroform), nondetects would not have resulted in additional exceedances of TEDF WAC based on maximum anticipated VOC hold-time bias (i.e., MDL multiplied by maximum hold-time bias is less than TEDF WAC). Additional exceedances of the chloroform WAC likely occurred for reported concentrations above the contaminant's MDL. Although not reflected in the routine-monitoring data, the WAC for bromodichloromethane was likely exceeded on one or more occasions among the 16 results reported above its MDL based on low VOC bias.

4.5 Waste Stream Dynamics Tests

Waste stream dynamics tests were conducted to evaluate the dilution, dispersion, and retention properties of facility waste streams for materials flowing from a single point of release (i.e., a facility) to end-of-pipe. Information from these tests is used to establish relationships between the chemistry of facility effluents, the physical properties of a facility waste stream, the configuration of the process sewer system, and the chemistry of the waste stream at end-of-pipe. Thus, these results are useful for

Table 4.8. Relationship Between Treated Effluent Disposal Facility Waste Acceptance Criteria and 1994 and 1995 Routine-Monitoring Data for Volatile Organic Compounds Measured at End-of-Pipe

Constituent	Frequency	Range	Method Detection Limit	Method Detection Limit x 3 ^(a)	Waste Acceptance Criteria
Bromodichloromethane	16/31	0.5-3.2	0.33	0.99	4
Chloroform	61/61	3.4-21	0.18	0.54	7
1,1-Dichloroethane	0/61	--	0.19	0.57	7
Methylene Chloride	39/61	0.2-1.6	0.16	0.48	5
Tetrachloroethene	1/61	2.0	0.70	2.1	9
Toluene	1/61	1.4	0.30	0.90	9
1,1,1-Trichloroethane	1/61	1.4	1.3	3.9	9
Trichloroethylene	7/61	0.32-0.7	0.32	0.96	3

(a) Estimated maximum concentration of nondetects based on the constituents method detection limit multiplied by the maximum anticipated volatile organic compound hold-time bias of 3.

interpreting routine-monitoring data and for predicting the impacts of facility releases on end-of-pipe chemistry. Such predictions could be very important in responding to significant releases, where there might be concern for violating TEDF's National Pollutant Discharge Elimination System permit or damaging TEDF's waste treatment trains.

4.5.1 Dye Behavior in Facility Waste Streams

Figure 4.7 displays representative end-of-pipe fluorescence profiles associated with dye releases in the absence (3720 Building) and presence (331 Building) of sump activity. Similar profiles were also obtained from tests conducted at two other buildings (i.e., profiles from tests at 324 Building resembled those from tests at 3720 Building, and profiles for 320 Building were similar to those from 331 Building).

Normally, each dye release at 3720 and 324 Buildings resulted in a single peak (observed initially at the building and later at end-of-pipe, Figure 4.7a) from which travel time parameters and dilution factors were calculated. However, the data from tests at 320 and 331 Buildings and the basement sump in 3720 Building were more complex. Multiple peaks with decreasing intensities were observed at end-of-pipe following each dye release (Figure 4.7b). This behavior appears to be a result of the incomplete removal of liquid from sumps. When a sump is pumped down, most of the sump's contents flow downstream toward end-of-pipe. However, any residual dye in the sump is diluted as the sump refills. After refilling, the sump is pumped down again, and a more dilute solution of dye is eventually detected at end-of-pipe. This cycle continues until all of the dye has been removed from the sump. The 320 and 331 Buildings both have sumps in-line with end-of-pipe. The 320 Building has a basement sump that collects effluent from the building's laboratories, and the sump affecting 331 Building is at the 3906 lift station, which is located southeast of 315 Building.

4.5.2 Arrival and Transit Times

The average and range of arrival and transit times (see definitions in Section 3.3.2) for the four buildings are listed in Table 4.9, and the transit times are plotted in Figure 4.8a. Generally, the transit times were about 4 to 8 minutes greater than the arrival times. However, this might not be the case for real contaminants, which could be released at different rates than the dyes. The 331 Building had the longest transit time of 4 hours and 21 minutes (for the primary dye peak), while the shortest transit time (47 minutes) was found at 3720 Building. For all four buildings, the values are consistent with the length of pipe between each facility and end-of-pipe. However, the high flow rate of the 324 Building process sewer (i.e., 50 gal/min) resulted in a transit time that was almost as short as that of the 3720 Building, which has a shorter flow path but a much lower flow rate (approximately 2 gal/min).

The 331 and 3720 Buildings had the largest variations in transit times. The ranges were greater than the corresponding average transit times. These fluctuations were primarily attributed to the activation of sump pumps and fluctuations in the process sewer flow rates.

4.5.3 Clearance Times

The average clearance times at the facilities and end-of-pipe are shown in Figure 4.8b and are listed in Table 4.10. For the 320, 324, and 3720 Buildings, the dye peaks were significantly narrower by the time they reached end-of-pipe. At 320 Building and in the sump-test at 3720 Building, the

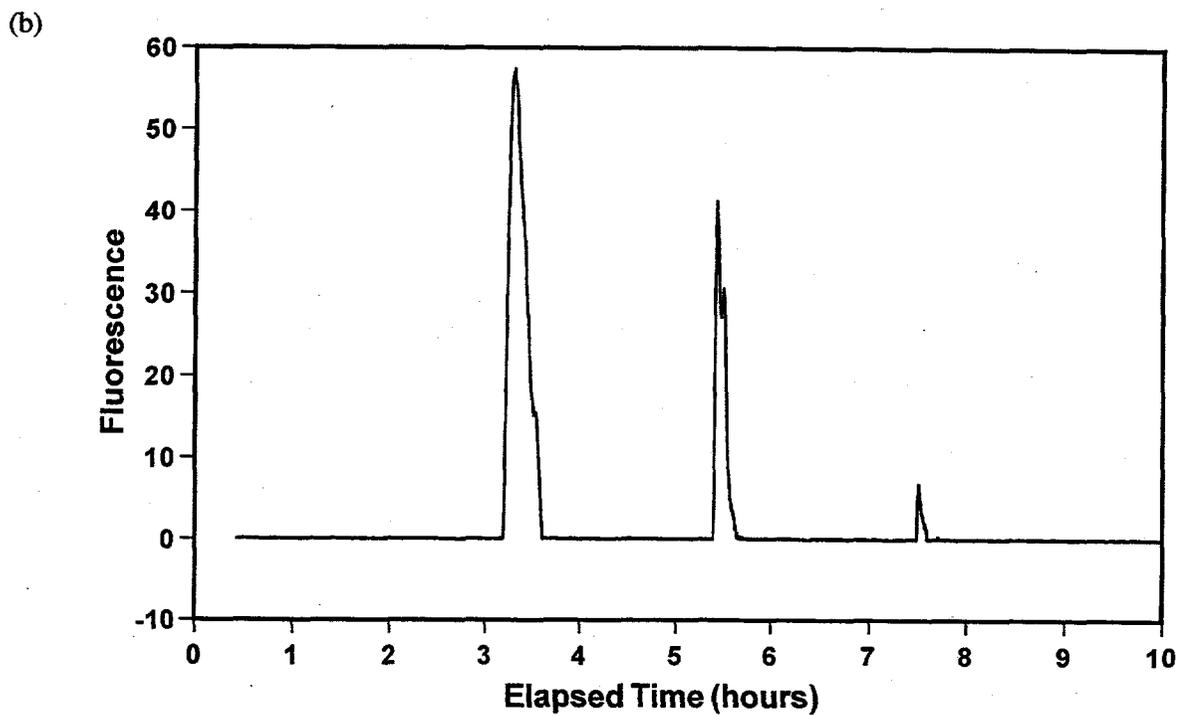
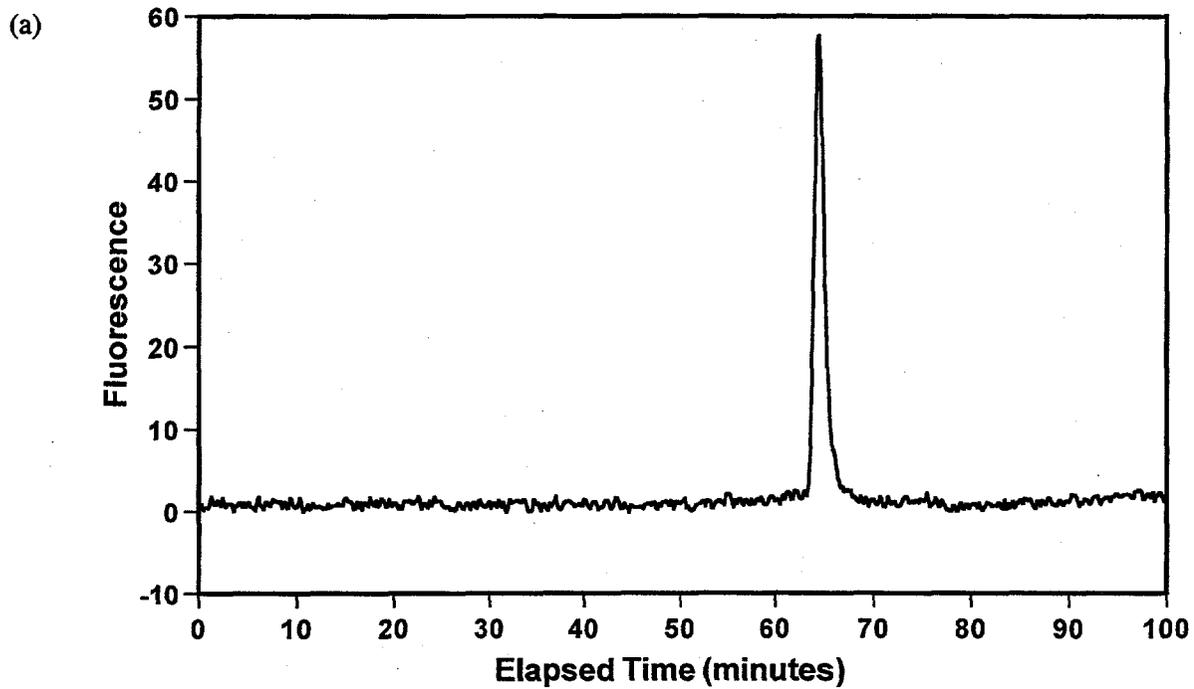


Figure 4.7. Representative End-of-Pipe Fluorescence Profiles of Dye Releases in the Absence (a) and Presence (b) of Sump Activity

Table 4.9. Arrival and Transit Times (Hours: Minutes)

Building	Parameter	Primary Dye Peak		Secondary Dye Peak		Tertiary Dye Peak ^(a)		Quaternary Dye Peak ^(a)	
		Average	Range	Average	Range	Average	Range	Average	Range
320	Arrival Time	1:49	1:28 - 2:02	2:26	2:23 - 2:28	3:01	2:43 - 3:18	3:58	3:44 - 4:13
	Transit Time	1:55	1:32 - 2:08	2:31	2:28 - 2:33	3:06	2:49 - 3:22	4:03	3:48 - 4:18
324	Arrival Time	0:47	0:33 - 0:53	--	--	--	--	--	--
	Transit Time	0:51	0:36 - 0:58	--	--	--	--	--	--
331	Arrival Time	4:13	2:38 - 7:30	6:16	3:35-10:53	7:59	6:06-10:34	--	--
	Transit Time	4:21	2:51 - 7:36	6:20	3:39-10:55	8:01	6:07-10:36	--	--
3720	Arrival Time	0:43	0:18 - 1:12	--	--	--	--	--	--
	Transit Time	0:47	0:19 - 1:25	--	--	--	--	--	--
-sump ^(b)	Arrival Time	0:27	--	2:11	--	3:57	--	--	--
	Transit Time	0:30	--	2:12	--	3:58	--	--	--

(a) Third and fourth peaks were not observed in all tests at the 331 and 320 Buildings, respectively.
 (b) Results are from the 3720 Building test involving a dye release into the basement sump.

building clearance times were relatively long (i.e., several hours), because the dye was either released directly into a sump (3720 Building) or was immediately collected in a sump after the dye was released. The sumps at both locations were emptied and refilled several times before the concentration of dye fell below the building fluorometer's detection limit. The 331 Building had the largest change in clearance times and was the only location that had an increase at end-of-pipe. Here, the 3906 lift-station sump resulted in an average clearance time of 4 hours, 23 minutes.

Another factor that could influence clearance times is chemical interaction by some contaminants (e.g., adsorption of metals on a pipe). Because the fluorescent dyes are relatively inert, such interactions should not have influenced these results.

4.5.4 Dilution Factors

Dilution factors for the four facilities are summarized in Table 4.11 and Figure 4.9. The 324 Building, with its high flow rate, had the smallest average dilution factor of 9.7. The average dilution factor at 3720 Building was 42, and the values had large fluctuations (i.e., 7.6 to 77). In large part, these variations appear to be caused by the increased flow rate associated with the emptying of the building's basement sump, because much lower dilution factors were observed when the timing of the dye release coincided with the emptying of the sump. A relatively low dilution factor of 28 was also

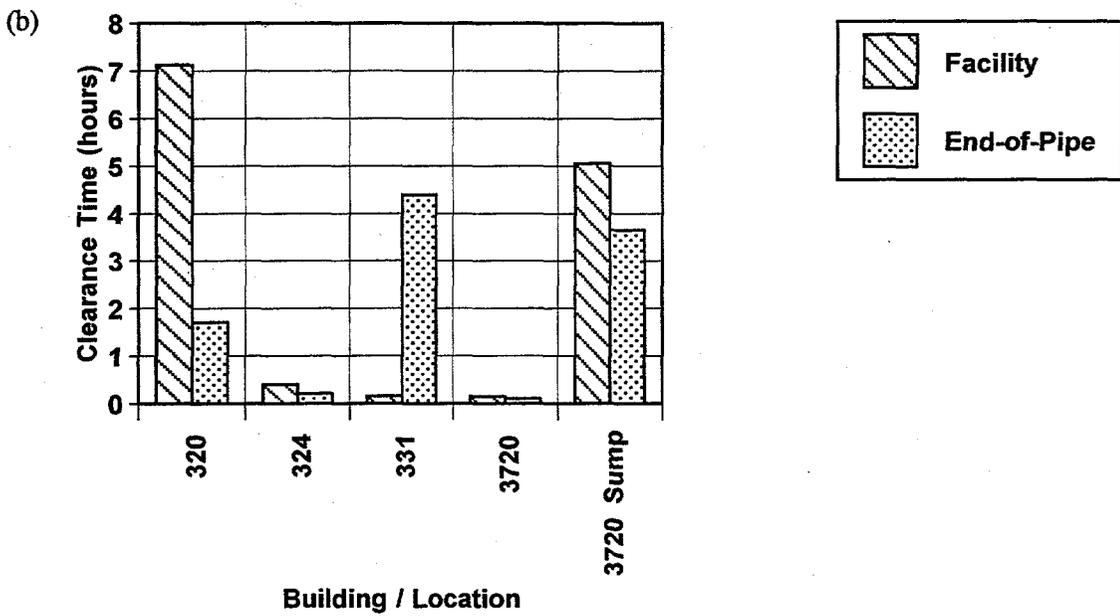
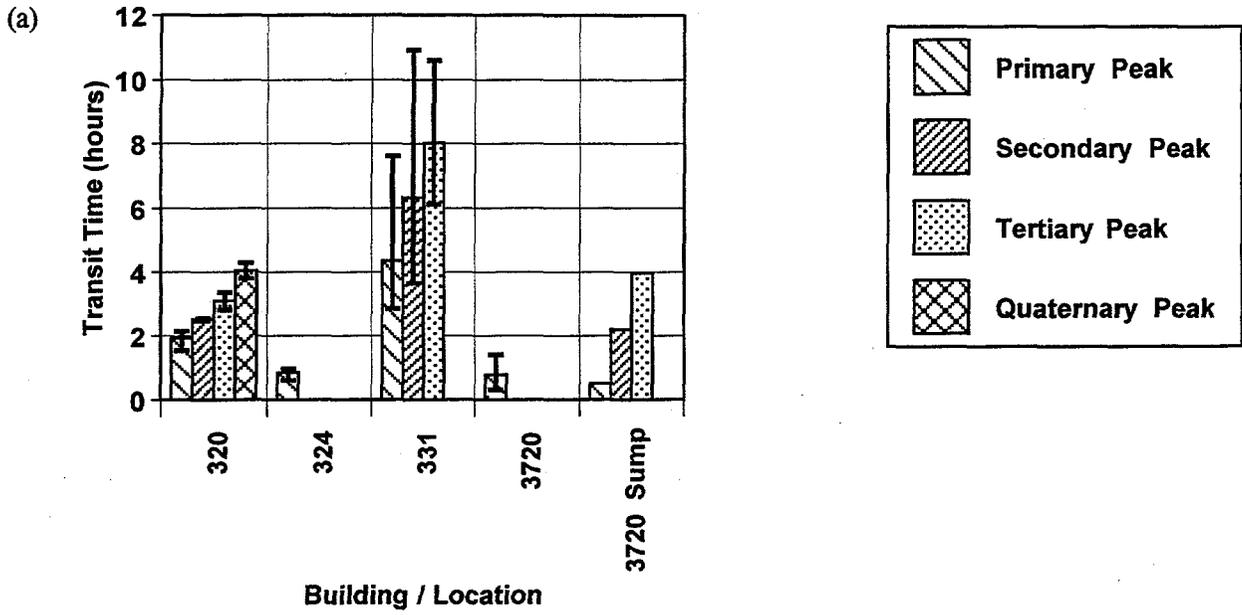


Figure 4.8. Transit (a) and Clearance (b) Times for Selected 300 Area Buildings

Table 4.10. Average Clearance Times

Building/Location	At the Building/Location	At End-of-Pipe	Relative Change (%)
320	7 hr 7 min	1 hr 42 min	-76.1
324	23 min 30 s	12 min 16 s	-47.8
331	9 min 12 s	4 hr 23 min	2760
3720	8 min 43 s	5 min 44 s	-34.2
3720 sump	5 hr 3 min	3 hr 39 min	-27.7

Table 4.11. Dilution Factors

Building/Location	Primary		Secondary		Tertiary ^(a)		Quaternary	
	Average	Range	Average	Range	Average	Range	Average	Range
320	27	--	35	--	141	--	366	--
324	9.7	6.8 - 12.2	--	--	--	--	--	--
331	524	471 - 616	980	638 - 1561	3092	2893 - 3290	--	--
3720	42	7.6 - 77	--	--	--	--	--	--
3720 sump	28	--	135	--	417	--	--	--

(a) A third peak was not observed in every test at 331 Building.

observed for the primary dye peak in the 3720 Building sump test. The 320 and 331 Buildings had primary dilution factors of 27 and 524, respectively, and subsequent values as high as 366 (320 Building) and 3,290 (331 Building). In general, each pulse of dye created by the action of the sumps was approximately 2 to 5 times more dilute than its predecessor. Thus, for contaminant releases at these facilities (or from a basement laboratory in 3720 Building), the number of significant pulses at end-of-pipe will depend largely on the initial concentration of the contaminant. The initial concentration in such releases will also have a major influence on the end-of-pipe clearance time.

4.5.5 Waste Stream Transport and Attenuation of Rhodamine WT versus Hexone

Figures 4.10 shows the dye's fluorescence and hexone's concentration profiles at the 3720 Building and end-of-pipe sampling points. The fluorescence of rhodamine WT is proportional to the dye's concentration; thus, the graphs enable direct comparison of the two tracers. At the building sampling point, the hexone and dye peaks were nearly coincidental (Figure 4.10a), and their clearance times appeared to be approximately the same (19 minutes, 30 seconds for rhodamine WT). Discrepancies between the tracers' behavior are apparent in the end-of-pipe data (Figure 4.10b). A single peak was observed for the dye, while the hexone profile consisted of at least three peaks. Although more data points are necessary to fully characterize the hexone profile, the existing data shows that the two points of highest concentration lagged approximately 6.5 and 11.5 minutes behind the transit time of the dye

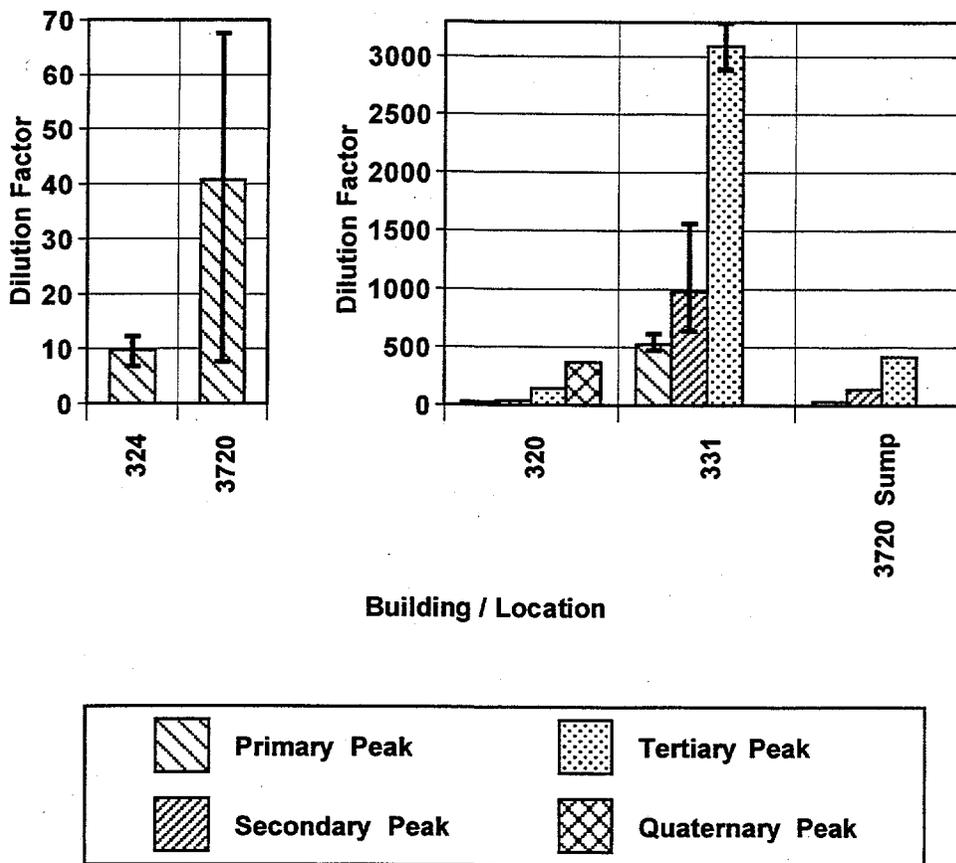


Figure 4.9. Dilution Factors for Selected 300 Area Building Waste Streams

(45.7 minutes). These differences in behavior may have been caused by interactions between hexone and the sewer system or other organic compounds present in the waste stream.

The dilution factors of the dye and hexone were similar, based on the maximum concentrations of the two largest hexone peaks. Rhodamine WT was diluted by a factor of 77, while the dilution factors for hexone were 75 and 66, respectively. These three values were higher than all of the other primary dilution factors obtained from tests at 3720 Building. However, the higher values were most likely caused by the flow conditions at the time of the test, rather than the use of hexone in the test.

Overall, these results show that the dye provides a conservative estimate on the travel time parameters and dilution factors of real waste stream contaminants (e.g., hexone). For compounds that undergo chemical interactions, transit and clearance times will be increased. In a similar fashion, dilution factors are expected to be similar to or greater than those observed for dyes, because of the influences of peak-broadening, volatilization, and possibly degradation.

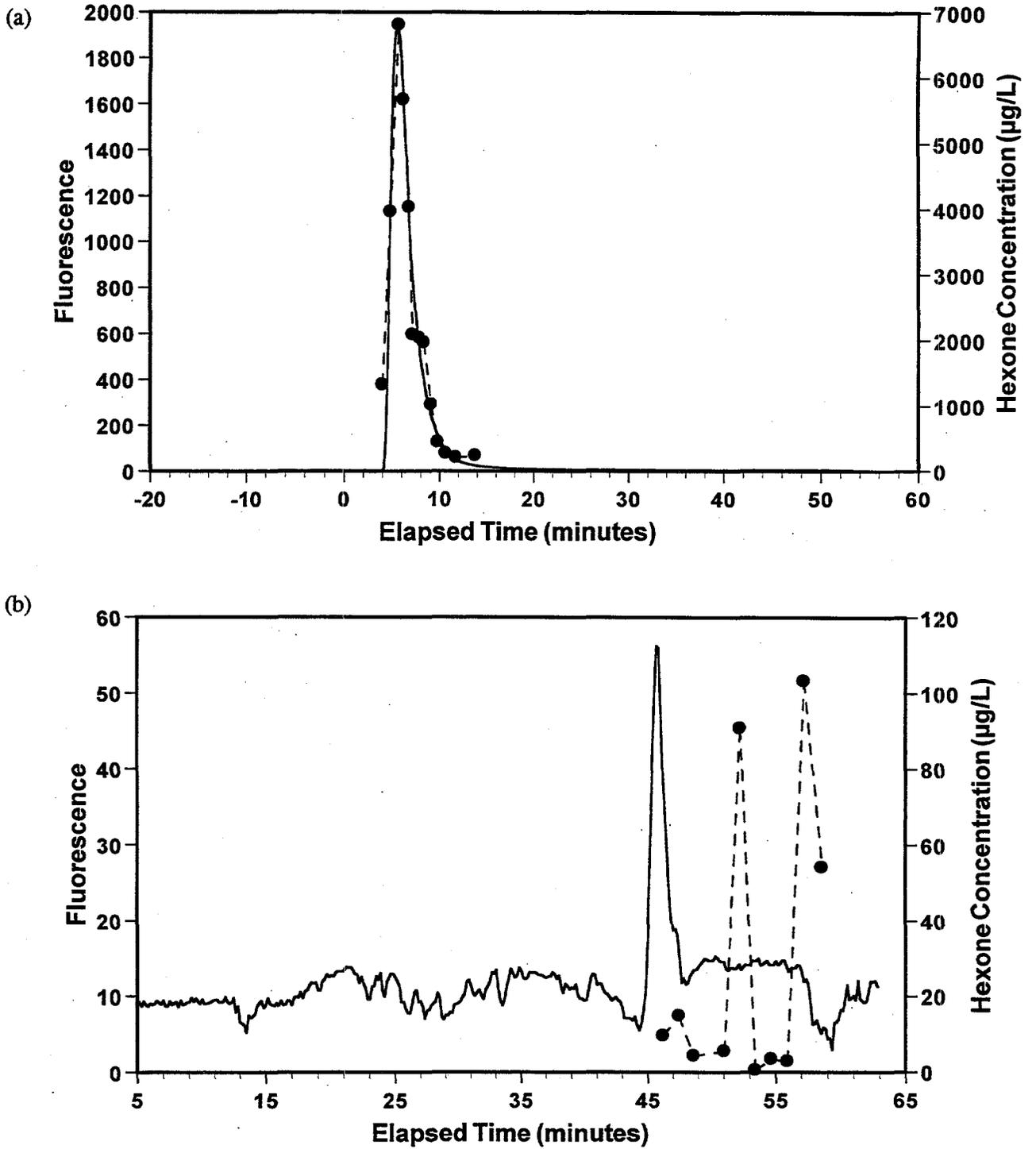


Figure 4.10. Dye Fluorescence and Hexone Concentration Profiles at 3720 Building (a) and End-of-Pipe (b). The dashed line/dark circles represent the hexone data, and the solid line denotes the fluorescence profile.

4.5.6 Effects of Waste Stream Dilution on Assessment of Facility Release Quantities

Facility release quantities have been calculated and summarized for a risk-dominant accident scenario (i.e., inadvertent spill of a hazardous chemical or radionuclide to a facility process sewer). For all calculations, a dilution factor of 757,000 was used assuming dilution by a half-full equalization tank at TEDF and that dilution by process sewer waste streams was insignificant. Our test has shown dilutions by the process sewer waste stream to range from 10 to 524 for facilities studied. Assuming the most conservative dilution, facility release quantities calculated could be reduced by at least a factor of 10 as a result of waste stream dilution that occurs between the facility release point and end-of-pipe.

5.0 Conclusions

Continuous monitoring of 331 Building pH, conductivity, and flow showed that almost all events that caused changes to those parameters occurred on weekdays during regular work hours. During events, pH ranged from 1.0 to 11.0, conductivity varied from 120 to 1,800 μ S, and flow spanned 3 to 50 gal/min. The duration of single events ranged from 5 to 50 minutes.

Two patterns of events that appeared to occur on a frequent basis were identified in the waste stream at 331 Building from event-triggered sampling. One pattern, commonly associated with elevated or high nitrate and phosphate concentrations and fluctuating pH, was attributed to cage and glass washing activities. This interpretation is consistent with facility operation staffs' description of this process chemistry. The other pattern was characterized by low to moderate conductivity, little pH change, and elevated or high copper, zinc, chloride, or sulfate content. It was suggested that this pattern may be the result of ongoing life sciences research activities. None of the events from either pattern showed elevated levels of chlorinated VOCs.

Event samples from 331 Building contained contaminant levels 1 to 2 orders of magnitude higher than those observed in composite samples collected as part of CY 1994 and CY 1995 routine monitoring activities. However, such levels, when associated with contaminants of concern, were predicted not to exceed TEDF WAC or EPA MCLs at end-of-pipe. Occasionally, concentrations of nitrate as high as 100 mg/L (i.e., 10 times greater than the MCL) were observed during CY 1994 and CY 1995 routine monitoring at end-of-pipe. These levels likely resulted from concentrated releases from one or more facilities containing contaminant levels significantly above those observed in the field test.

In the field test, event samples containing high levels of acetone and isopropyl alcohol were accompanied by very low pH and conductivity responses. Thus, events consisting of releases of high levels of organic compounds may go undetected when limited to current continuous monitoring capability.

Sample hold times associated with the field test (i.e., field, < 1 hour; on-site, 10 to 14 days; off-site, 23 to 27 days) significantly affected VOC data quality.

- The number of VOC analyses detected decreased in the order of in-field >> on-site > off-site. This was attributed to losses occurring during the sample transport and storage process. Benzene, carbon tetrachloride, 1,1-dichloroethane, 1,2-dichloroethane, *trans*-1,2-dichloroethene, and ethylbenzene were detected in field-analyzed samples but were not detected in CY 1994 and CY 1995 331 Building routine-monitoring samples. In the VOC hold-time study, none of these contaminants were detected in samples analyzed by the off-site laboratory, which performed most of the VOC analyses associated with CY 1994 and CY 1995 routine monitoring of 300 Area facility liquid waste streams. Thus, some VOC analyses likely went unreported in the CY 1994 and CY 1995 routine-monitoring data sets. However, of those compounds not detected in 331 Building routine-monitoring samples, only 1,1-dichloroethane is on the TEDF WAC. Nondetects of 1,1-dichloroethane would not have exceeded TEDF WAC when taking into account the effect of hold-time bias.

- VOC data from CY 1994 and CY 1995 routine monitoring of 300 Area building liquid waste streams is probably biased low (i.e., by a factor of 1.5 to 3) and most likely includes some false nondetects because of analyte losses incurred during the first 10 to 14 days of the sample transport and storage process. As a result of the low bias, some TEDF WAC for VOC were probably exceeded more frequently in CY 1994 and CY 1995 than the routine-monitoring data indicates. For example, 38% more chloroform exceedances might have been observed in CY 1994 and CY 1995 331 Building routine-monitoring data reported by the off-site laboratory were it not for losses that occurred during sample transport and storage. However, it was also shown that with the exception of chloroform and bromodichloromethane, no additional exceedances of TEDF WAC would have occurred in CY 1994 and CY 1995 routine-monitoring data for VOC at end-of-pipe when taking into account the influence of low bias. It should be noted that chloroform and bromodichloromethane are common constituents of treated (i.e., chlorinated) facility influent water and can account for exceedances of TEDF WAC for these constituents observed at end-of-pipe (Thompson et al. 1997, in press).
- A VOC event may go undetected if sample hold times are excessive. A chloroform event that occurred during the field test was clearly detected in samples analyzed within 13 days of collection but was barely discernable in a split sample analyzed 23 days after collection.

Concentrations, transit times, and clearance times for contaminants at end-of-pipe were highly dependent on the mechanical action of sumps and waste stream flow rates. Where present, the action of sumps had the greatest impact on contaminant clearance times. In the absence of sump activity, the waste stream flow rate was the controlling factor.

- Average transit times in the absence of sump activity were 47 minutes at 3720 Building and 51 minutes at 324 Building. In contrast, average transit times in the presence of sump activity were 1 hour, 55 minutes and 4 hours, 21 minutes at 320 and 331 Buildings, respectively. Characteristic of these longer transit times were the splitting of the dye profile into two to four discrete peaks that were observed as dye pulses at end-of-pipe. These discrete fractions were indicative of incomplete removal of liquid from the sumps during draw down cycles. The total number of dye pulses at end-of-pipe depended on the initial dye concentration.
- The high flow rate of the 324 Building process sewer (i.e., 50 gal/min) resulted in a transit time that was almost as short as the 3720 Building, which has a shorter flow path but a much lower flow rate (approximately 2 gal/min).
- Clearance times at 320, 324, and 3720 Buildings were less at end-of-pipe than at the building sampling points. However, for dye releases at 331 Building, the action of an intercepting sump resulted in a 2760% increase in the clearance time at end-of-pipe. This difference was likely due to sump location (i.e., at the facility as opposed to near end-of-pipe).

Dilution factors are valuable for predicting the impact of facility releases at end-of-pipe. Using the average dilution factor of 524 for 331 Building, it was estimated that four contaminants released from the 331 Building during monitored events would not exceed TEDF WAC or EPA MCL at end-of-pipe. Average dilution factors for 320, 324, 331, and 3720 Buildings were 27, 9.7, 524, and 42, respectively. It was also shown that the effect of waste stream dilution of a contaminant (i.e., dilution that

occurs between a facility release point and end-of-pipe) should be considered significant when calculating and assessing inventory release quantities associated with hazardous chemical and radionuclide spills to facility process sewers.

Comparison of the behavior of a fluorescent dye with that of hexone showed that the dye provides a conservative estimate on the travel time parameters and dilution factors of real waste stream contaminants.

To detect events that include organic chemicals, continuous monitoring for organic carbon could be adopted to complement pH and conductivity monitoring. Our finding that high concentrations of organic compounds (e.g., acetone and isopropyl alcohol) can escape detection based upon continuous monitoring of pH and conductivity alone is the basis for this conclusion.

Incorporation of event-triggered automated sampling could be used to limit analyses to those samples most likely to contain significantly elevated levels of contaminants (i.e., exceed TEDF WAC or EPA MCL) and that could identify weaknesses in administrative control practices. Composite sampling at weekly to bimonthly intervals, as practiced during CY 1994 and CY 1995 by the routine monitoring program, has limited chance of detecting events identified in one of these field tests.

The CY 1995 average off-site hold time for routine monitoring of samples for VOCs was 11 ± 5 days. When hold times (i.e., time from sample collection to sample analysis) exceed 10 days, VOC data should be interpreted realizing that not all VOC contaminants may have been detected and the analyte concentrations may have been significantly higher than the results indicate. Alternatively, on-site and off-site VOC analyses could be augmented by selected in-field VOC analyses to determine the amount of bias introduced in sample transport and storage process.

Additional dye tests on facility effluents would be of value so that the impacts of event releases to end-of-pipe for each 300 Area facility could be predicted. Analysis of targeted event samples revealed contaminant levels 1 to 2 orders of magnitude higher than the levels observed in 24-hr composite samples. Many of the concentrations were shown to exceed TEDF WAC or EPA MCL at the point of facility discharge. Concern as to whether these levels exceed TEDF WAC or EPA MCL at end-of-pipe could be readily addressed through the estimation capabilities of facility dilution models.

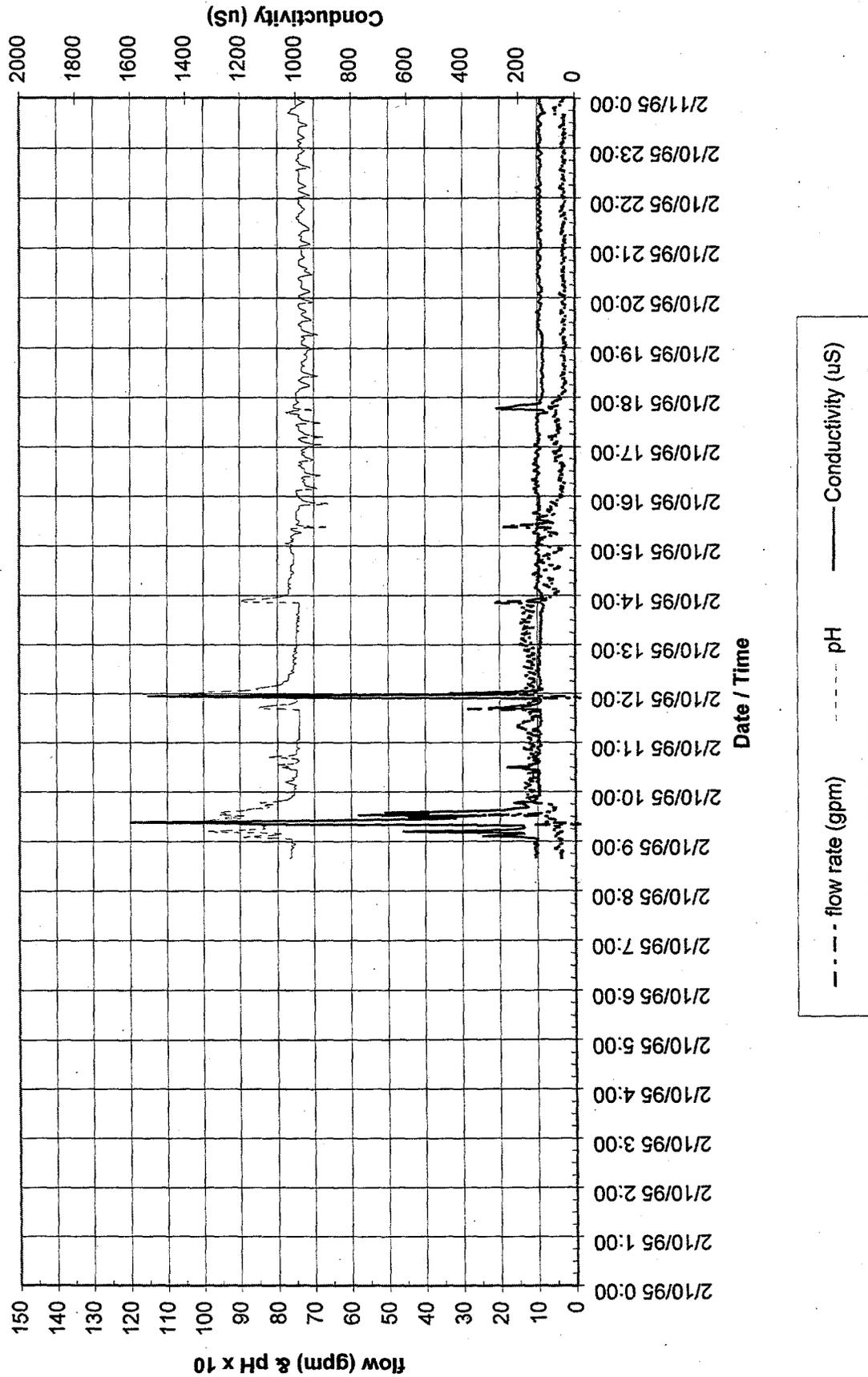
6.0 References

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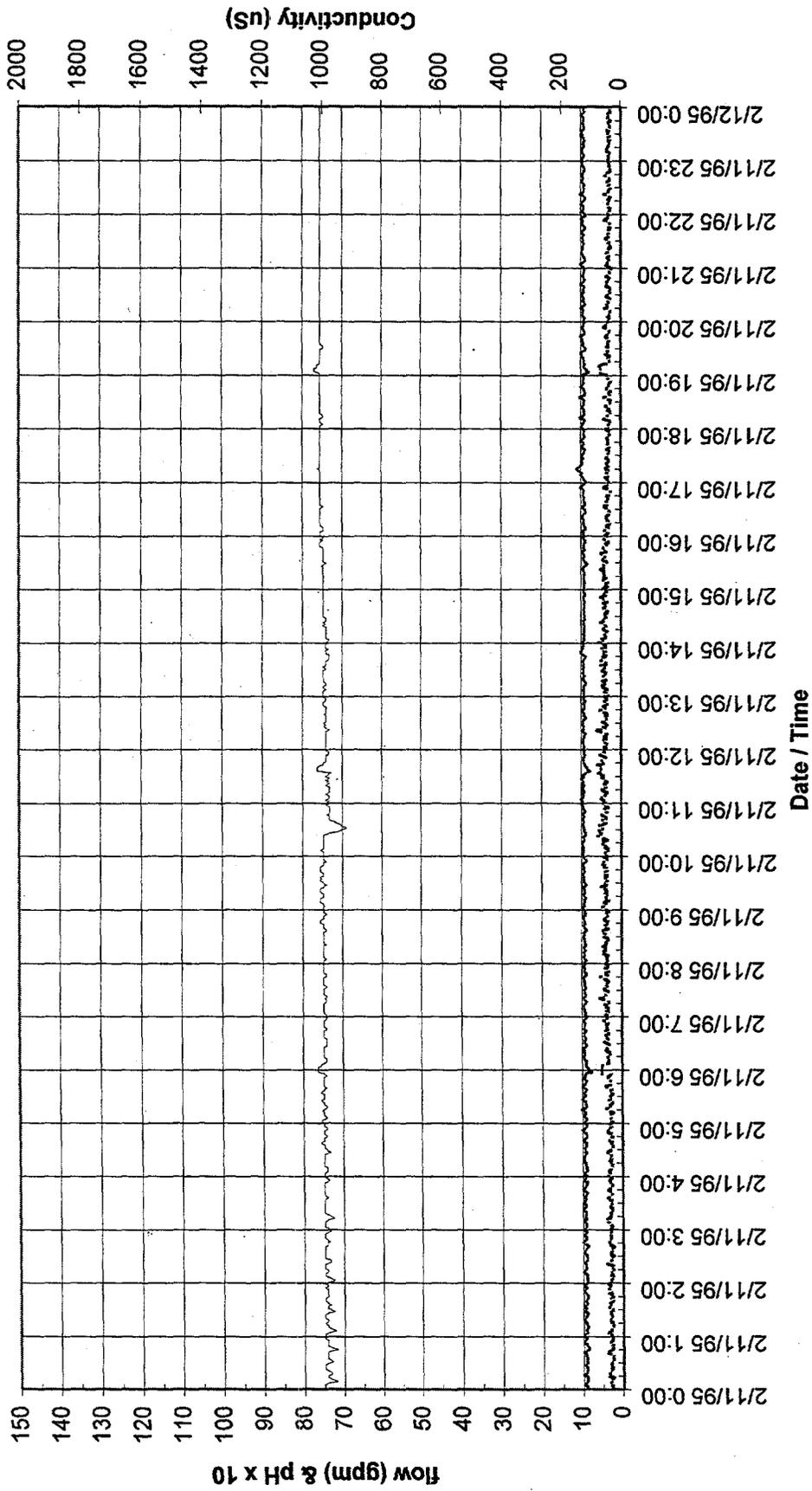
Appendix A

**Continuous Monitoring Data
February 11, 1995, through February 24, 1995**

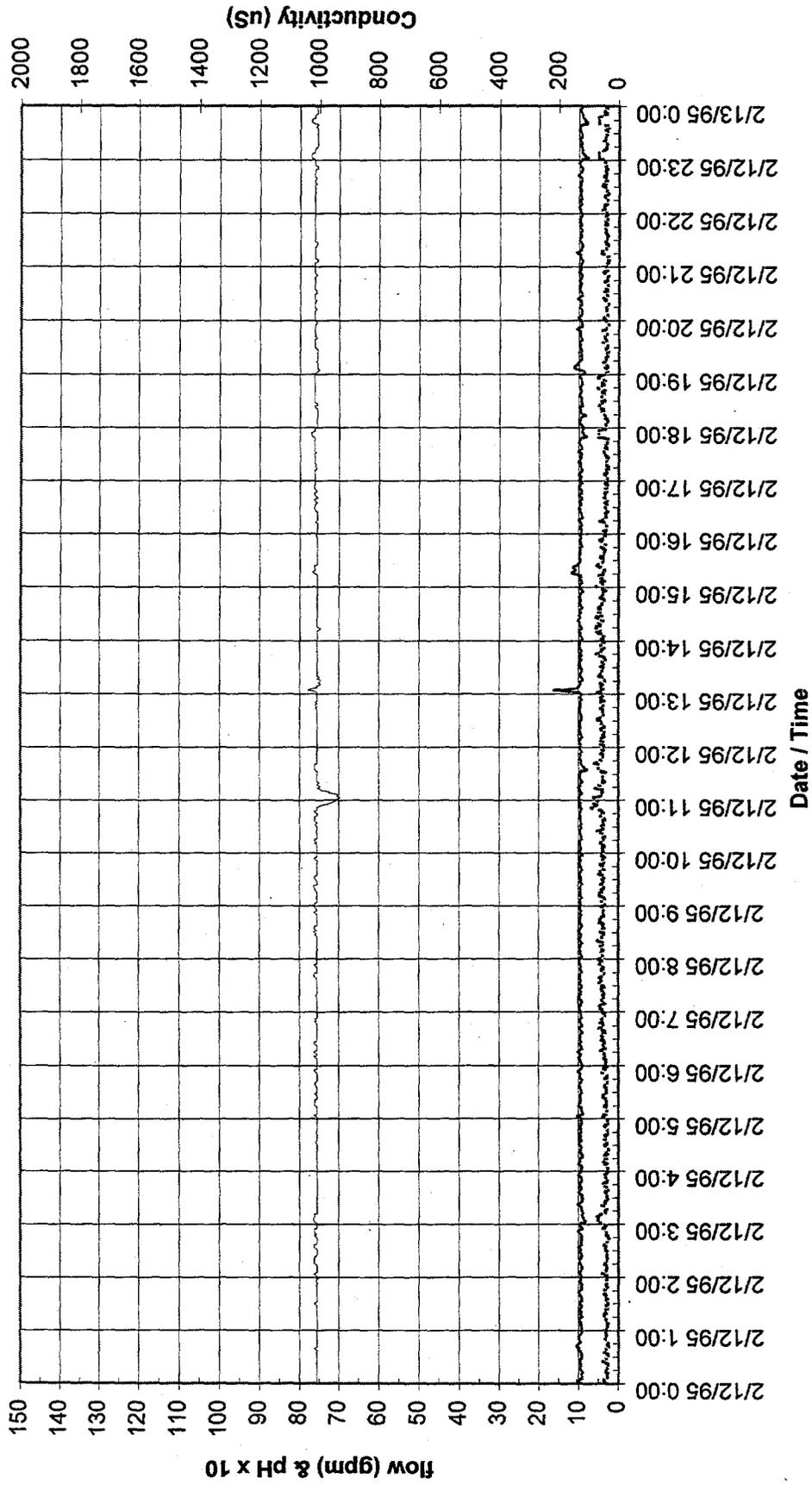
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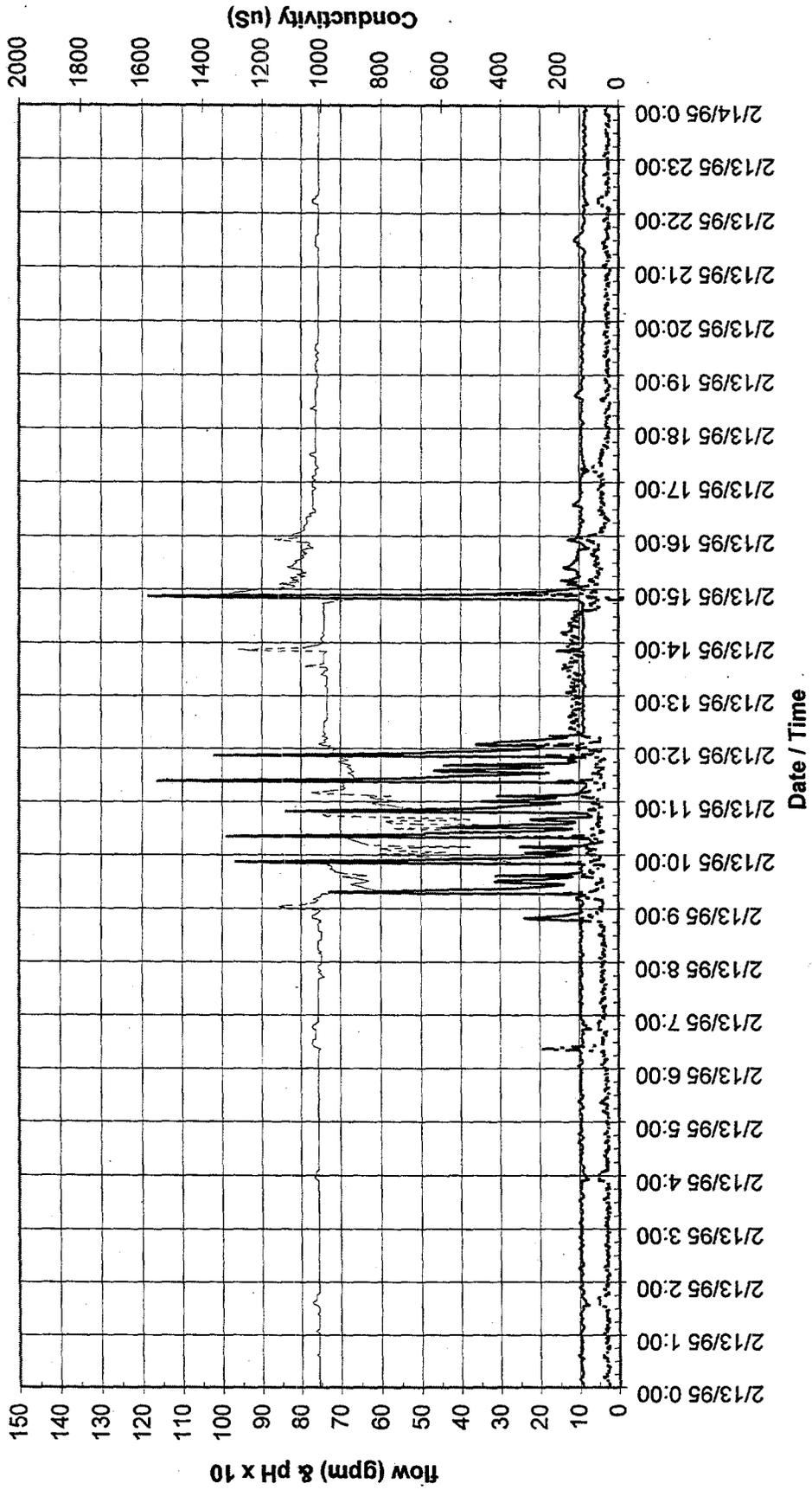
331 PS Data 11 Feb 95 (Saturday)



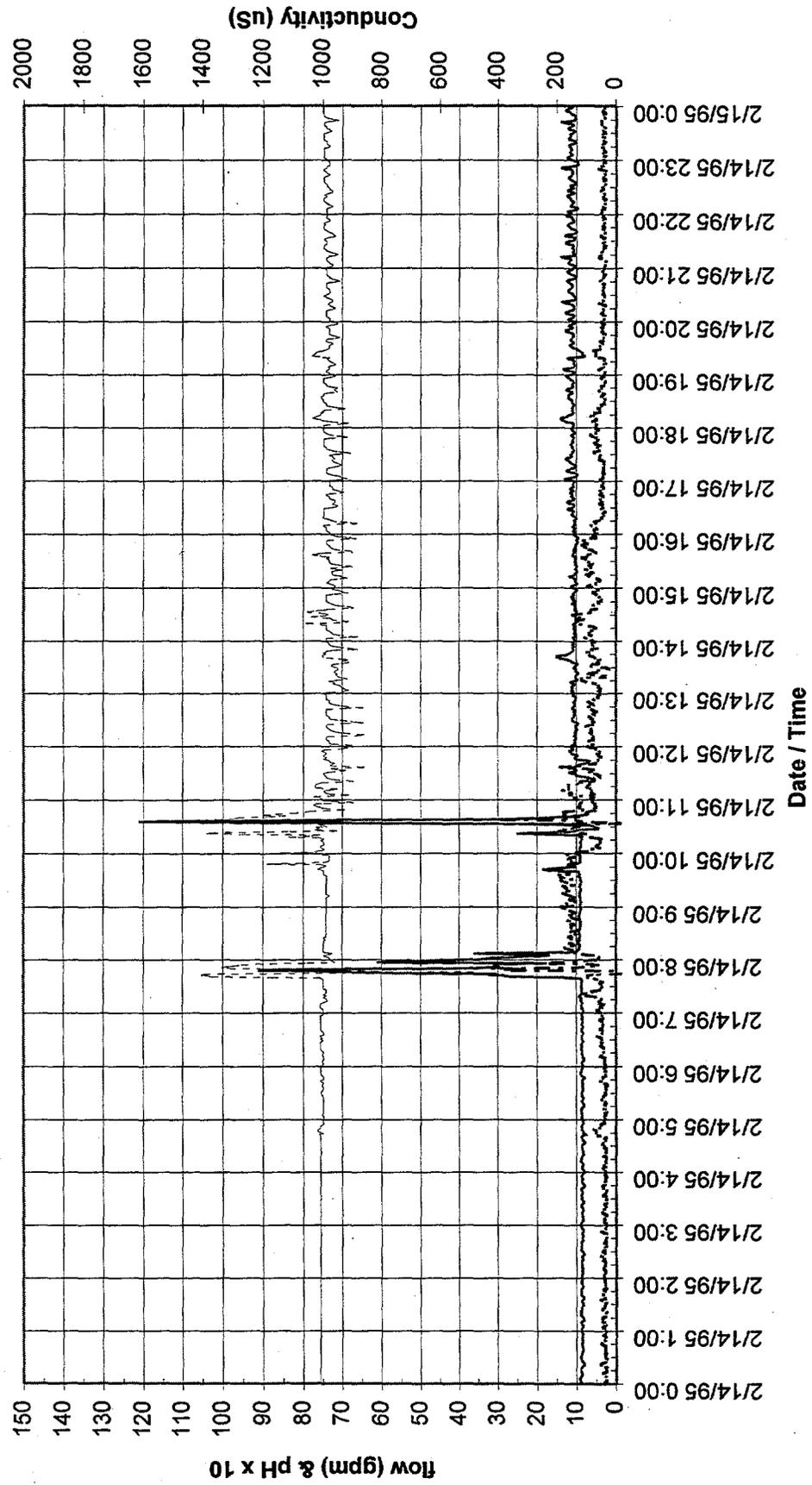
331 PS Data 12 Feb 95 (Sunday)



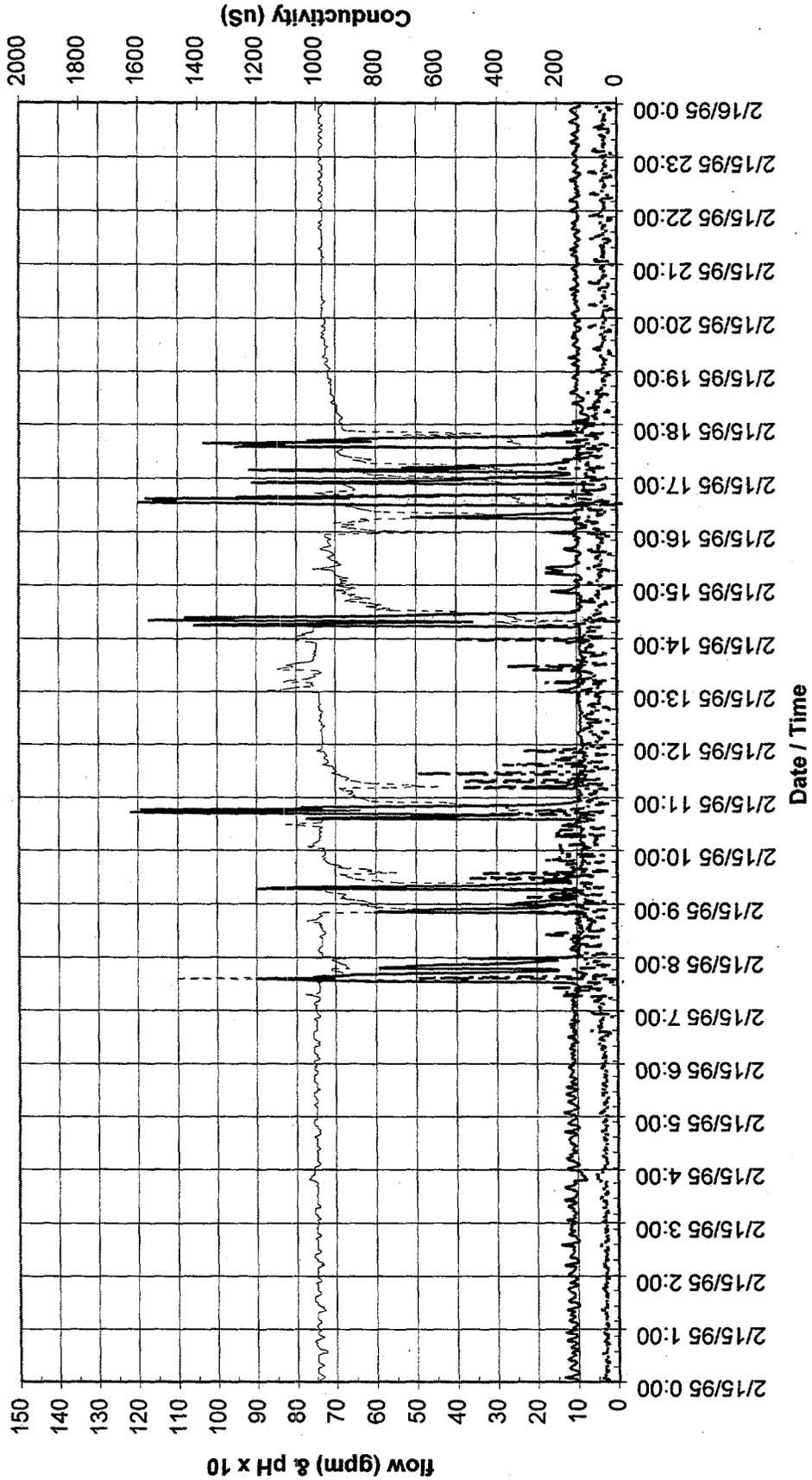
331 PS Data 13 Feb 95 (Monday)



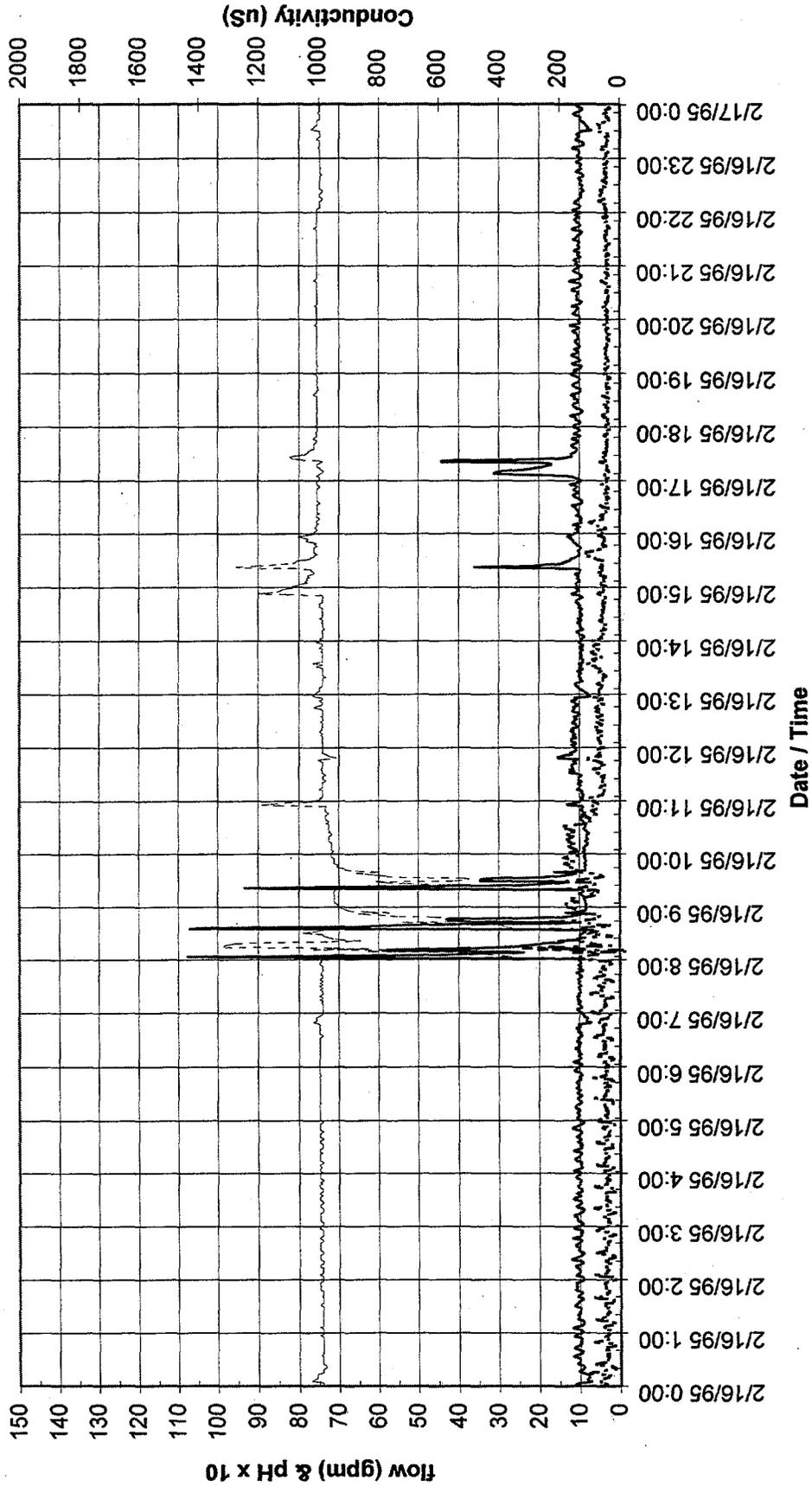
331 PS Data 14 Feb 95 (Tuesday)



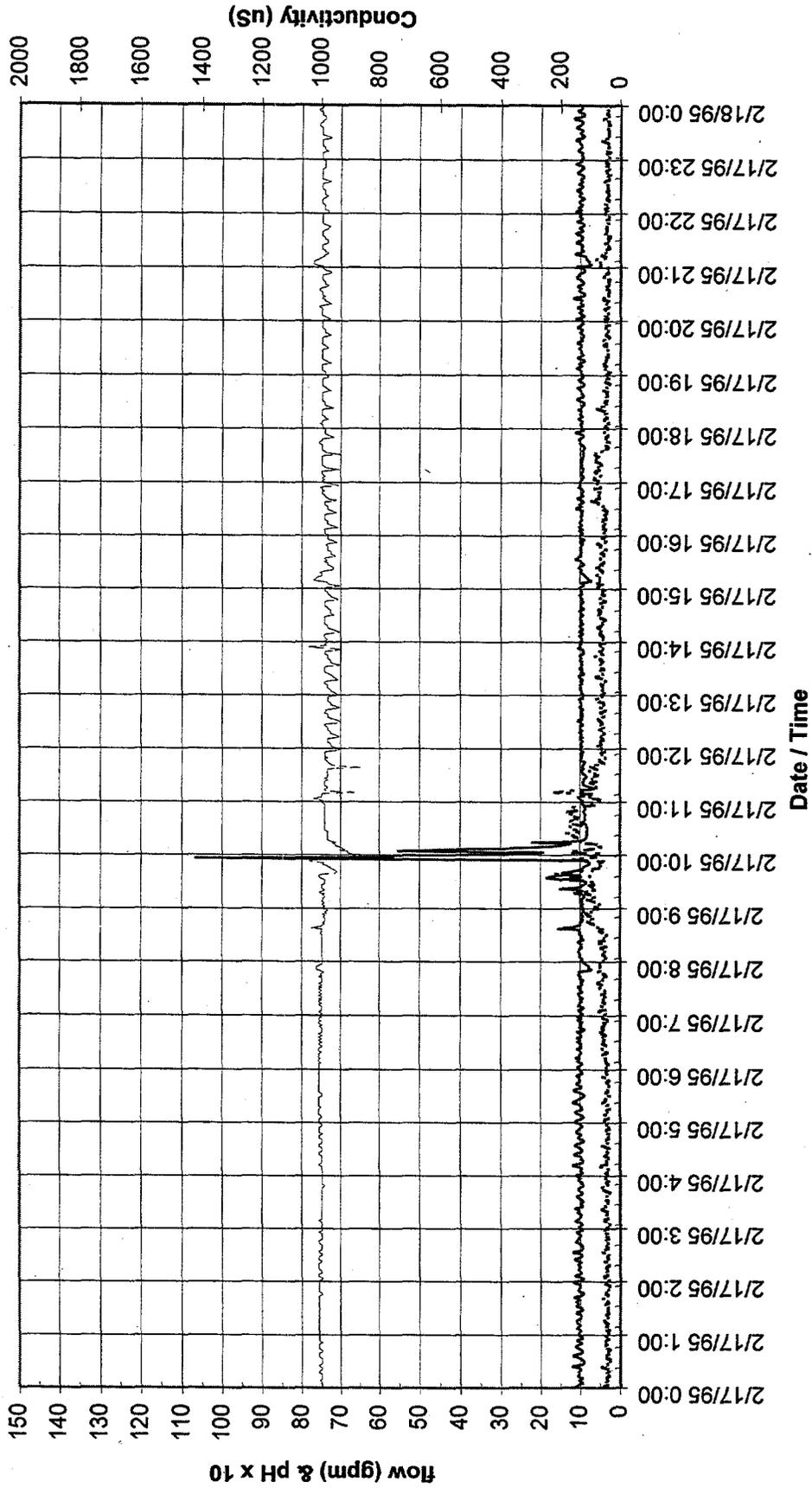
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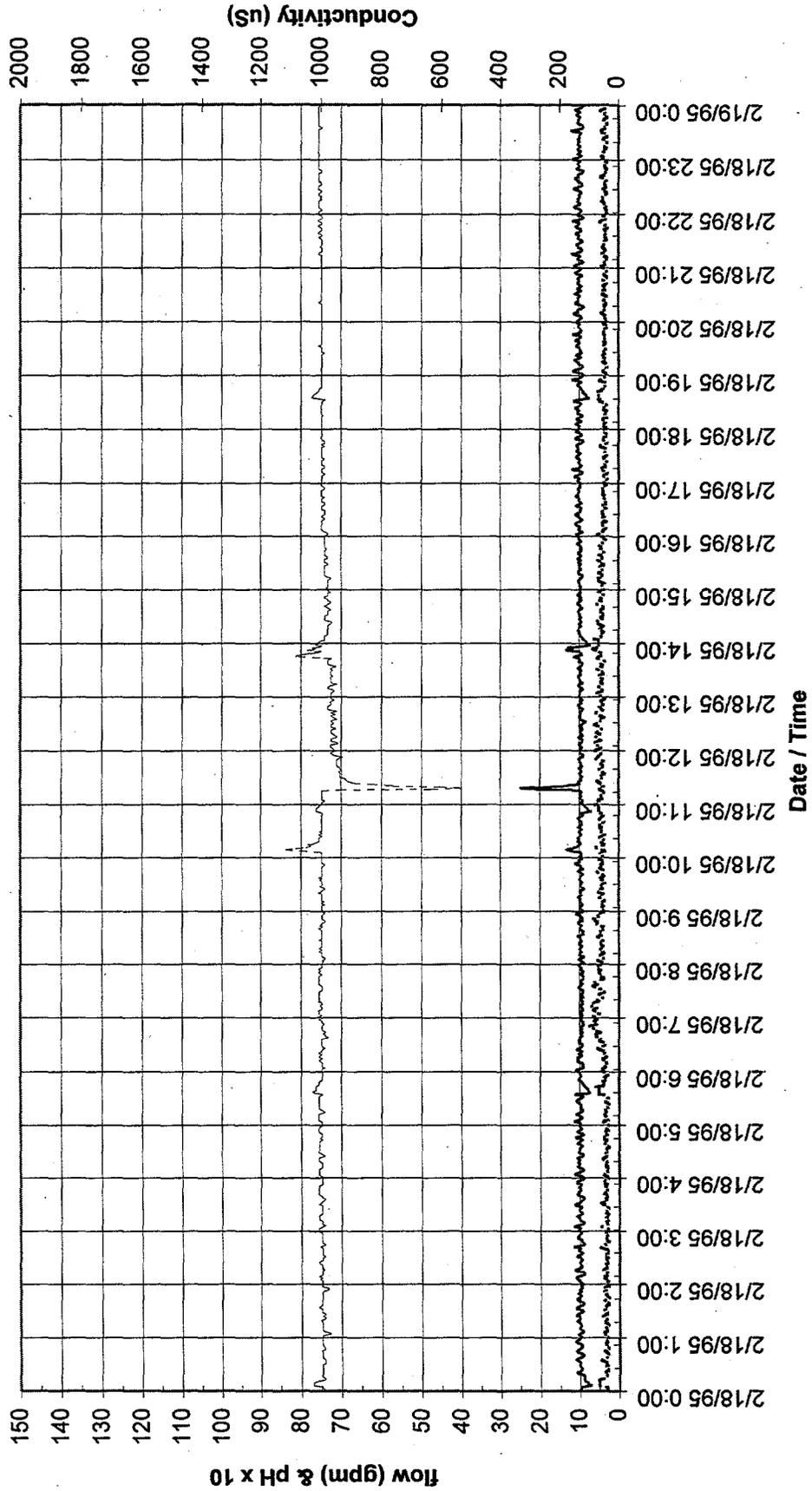
331 PS Data 16 Feb 95 (Thursday)



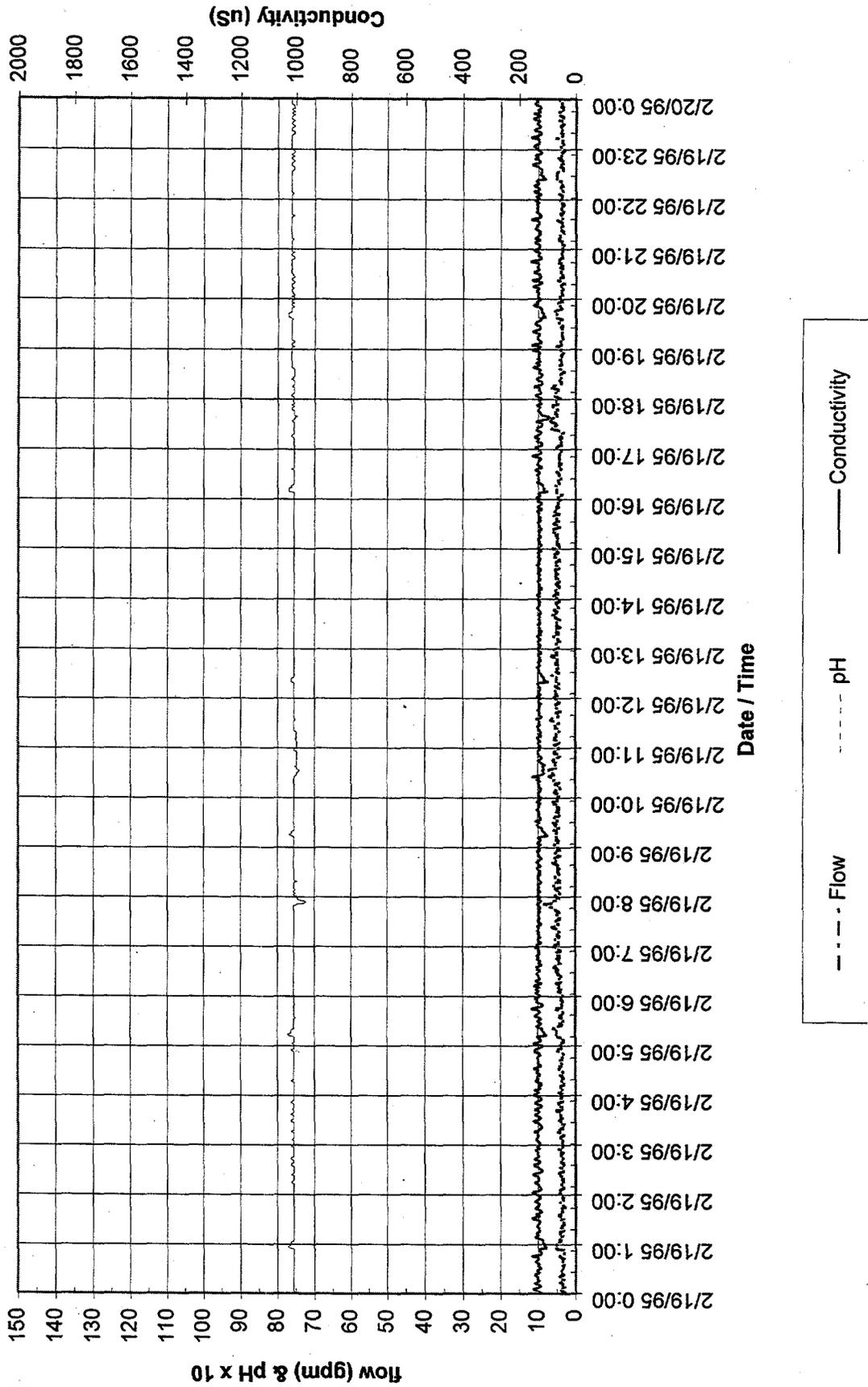
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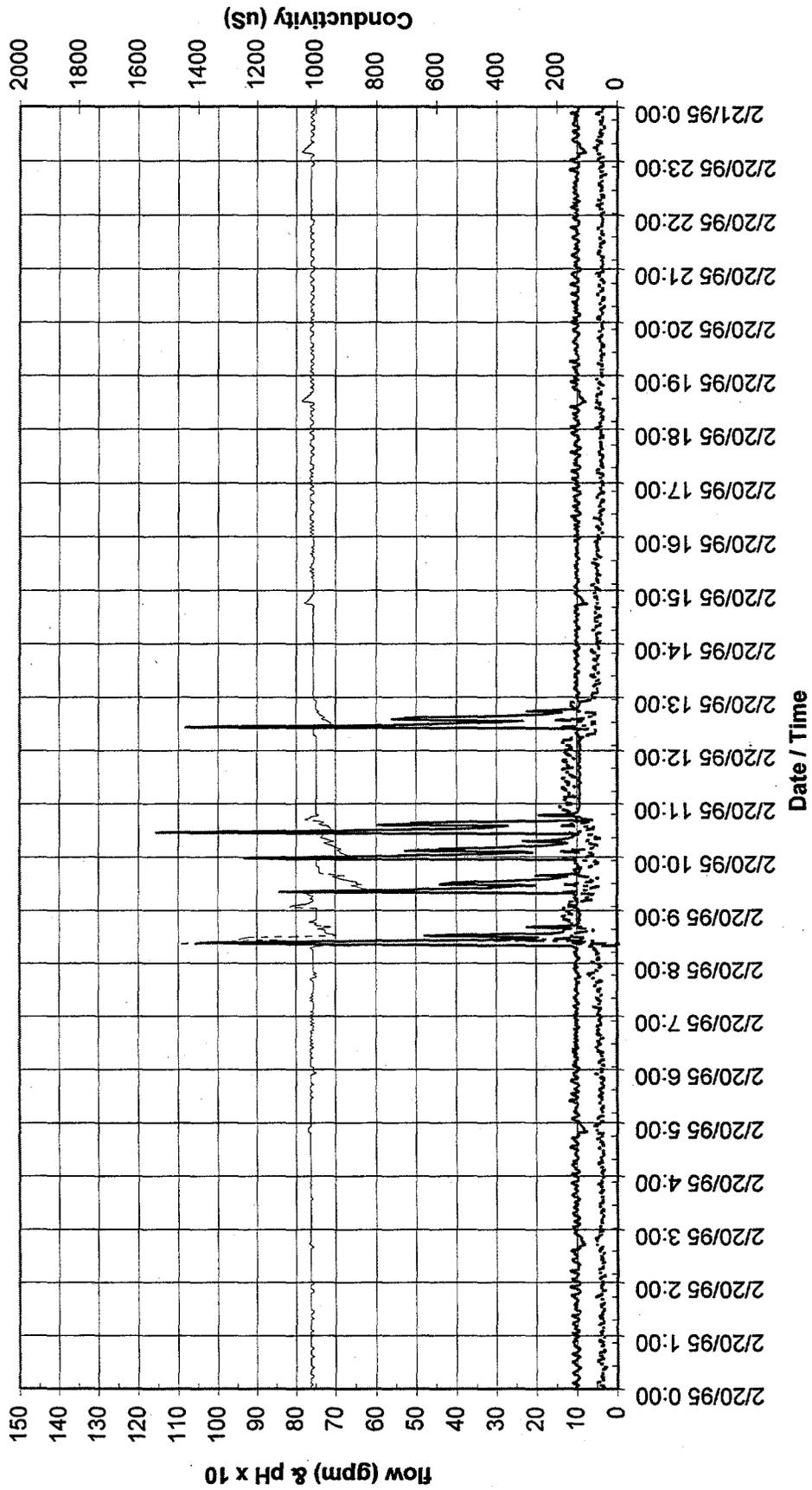
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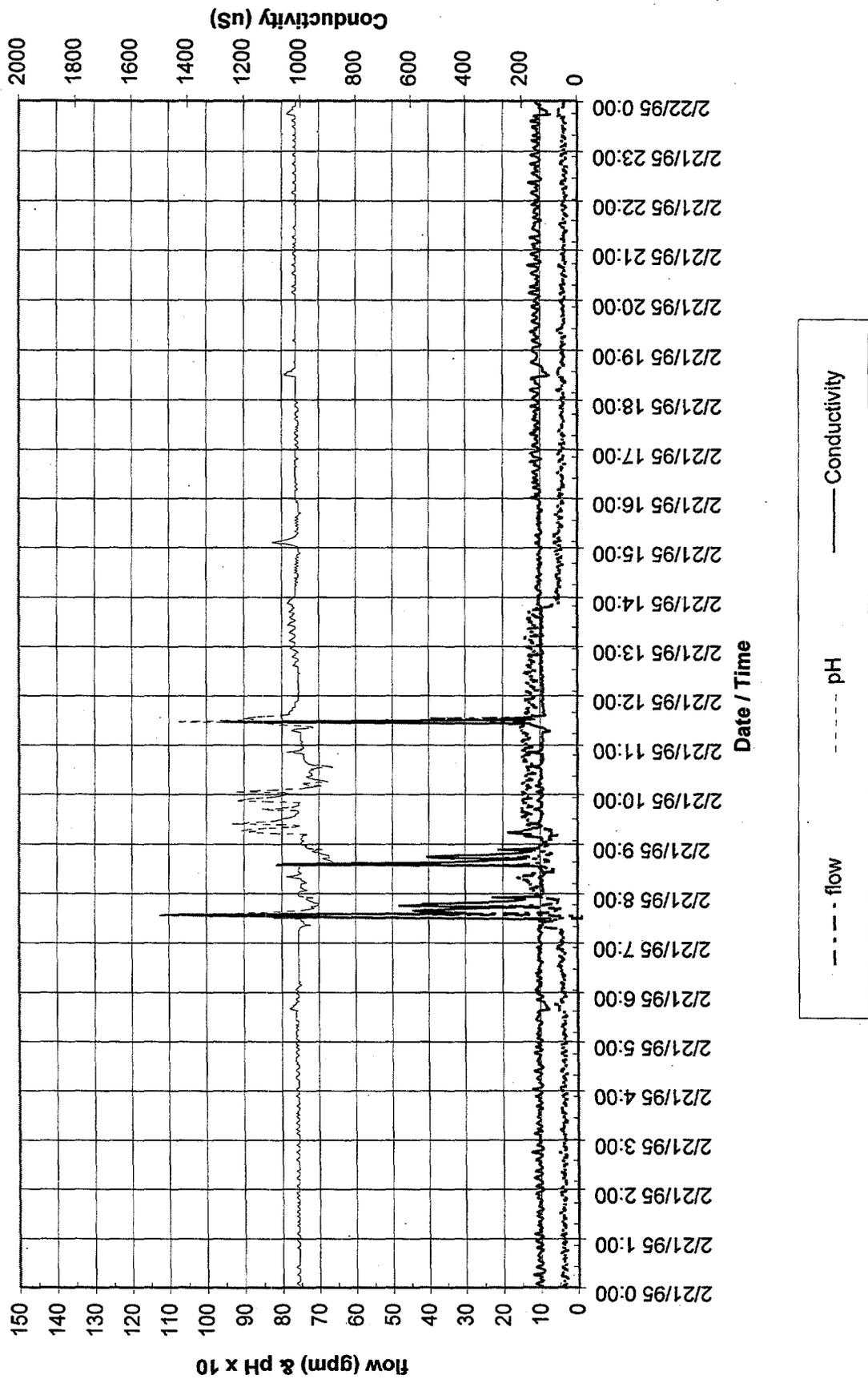
331 PS Data 19 Feb 95 (Sunday)



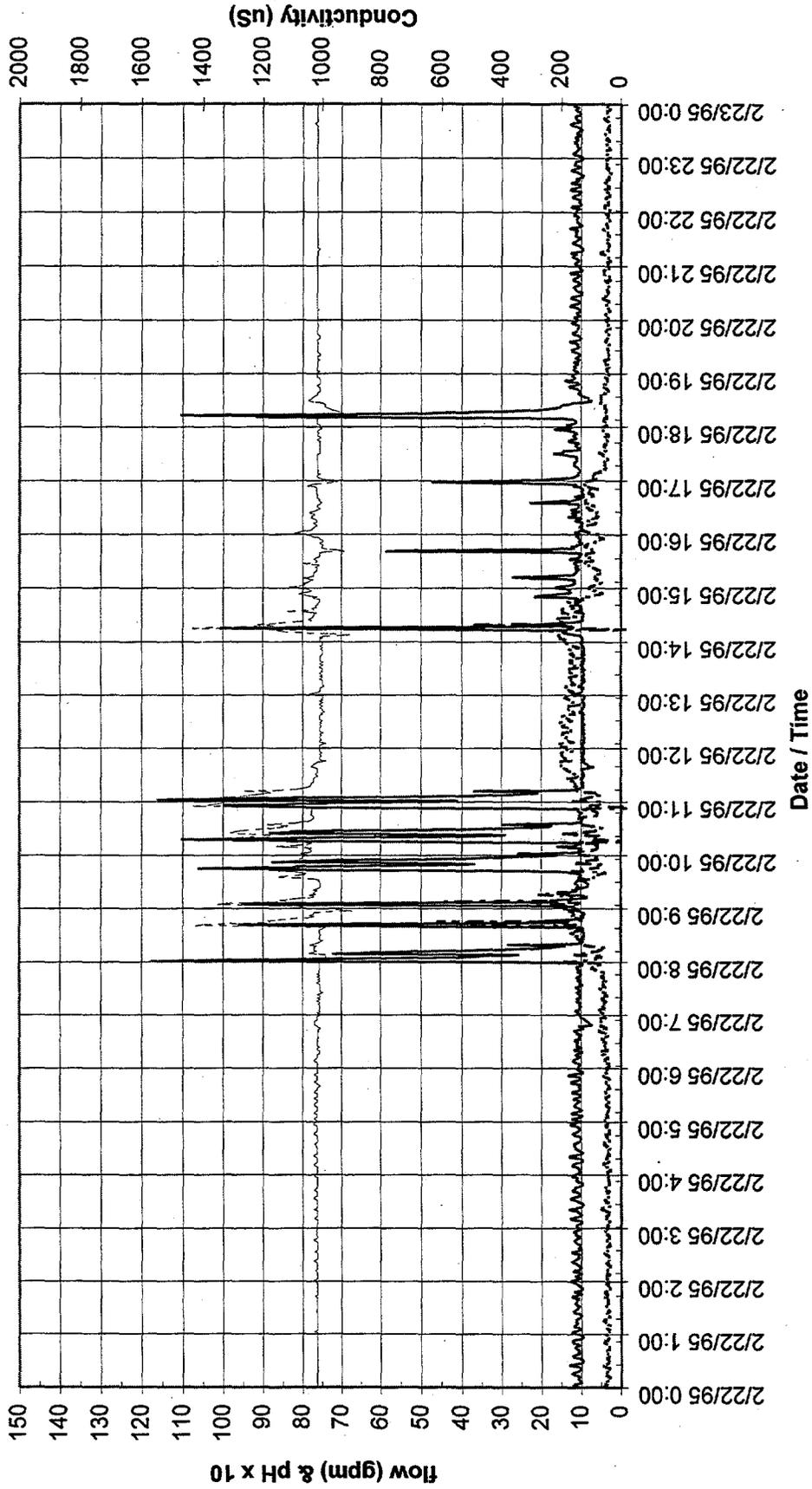
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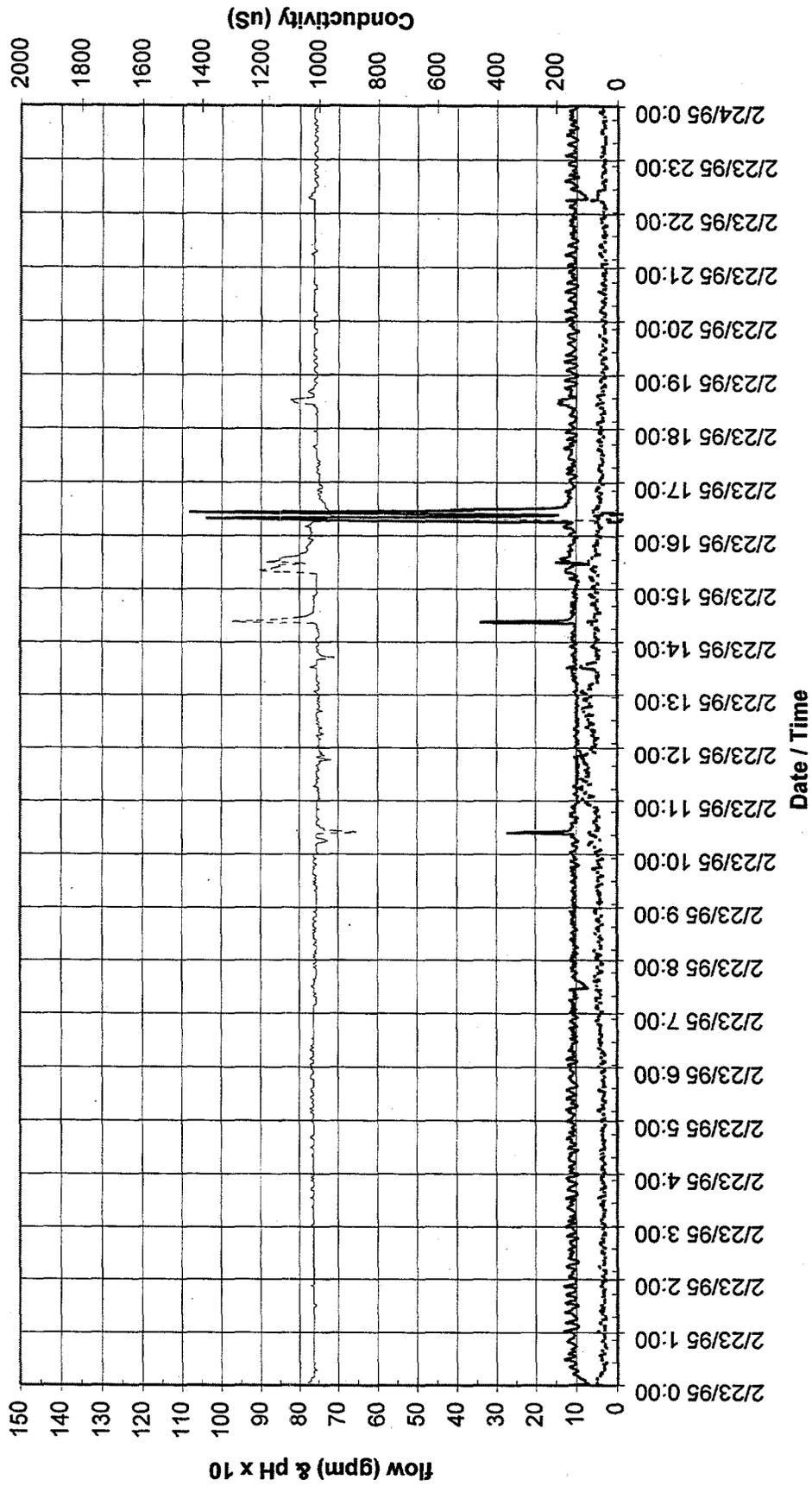
331 PS Data 21 Feb 95 (Tuesday)



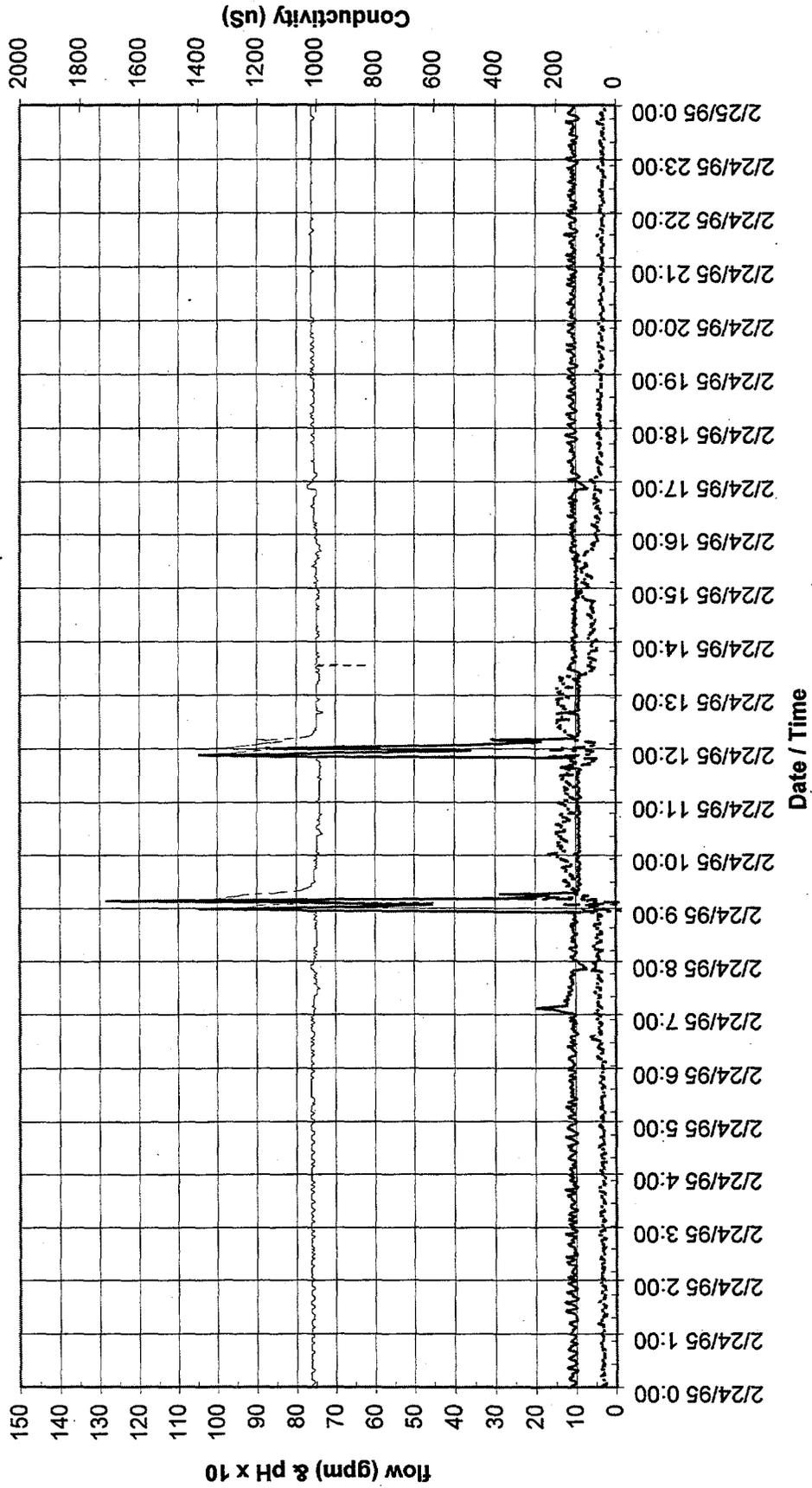
331 PS Data 22 Feb 95 (Wednesday)



331 PS Data 23 Feb 95 (Thursday)



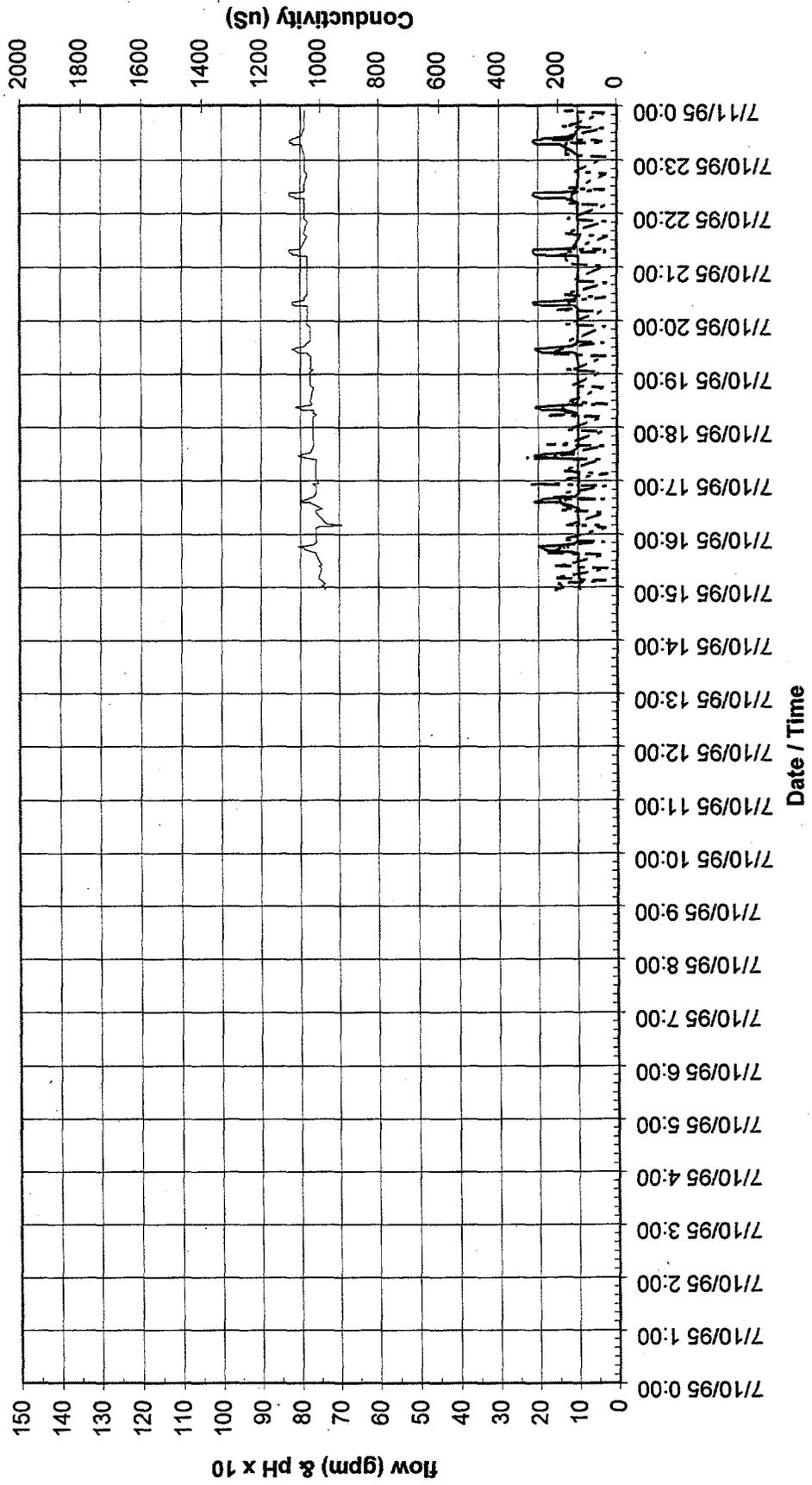
331 PS Data 24 Feb 95 (Friday)



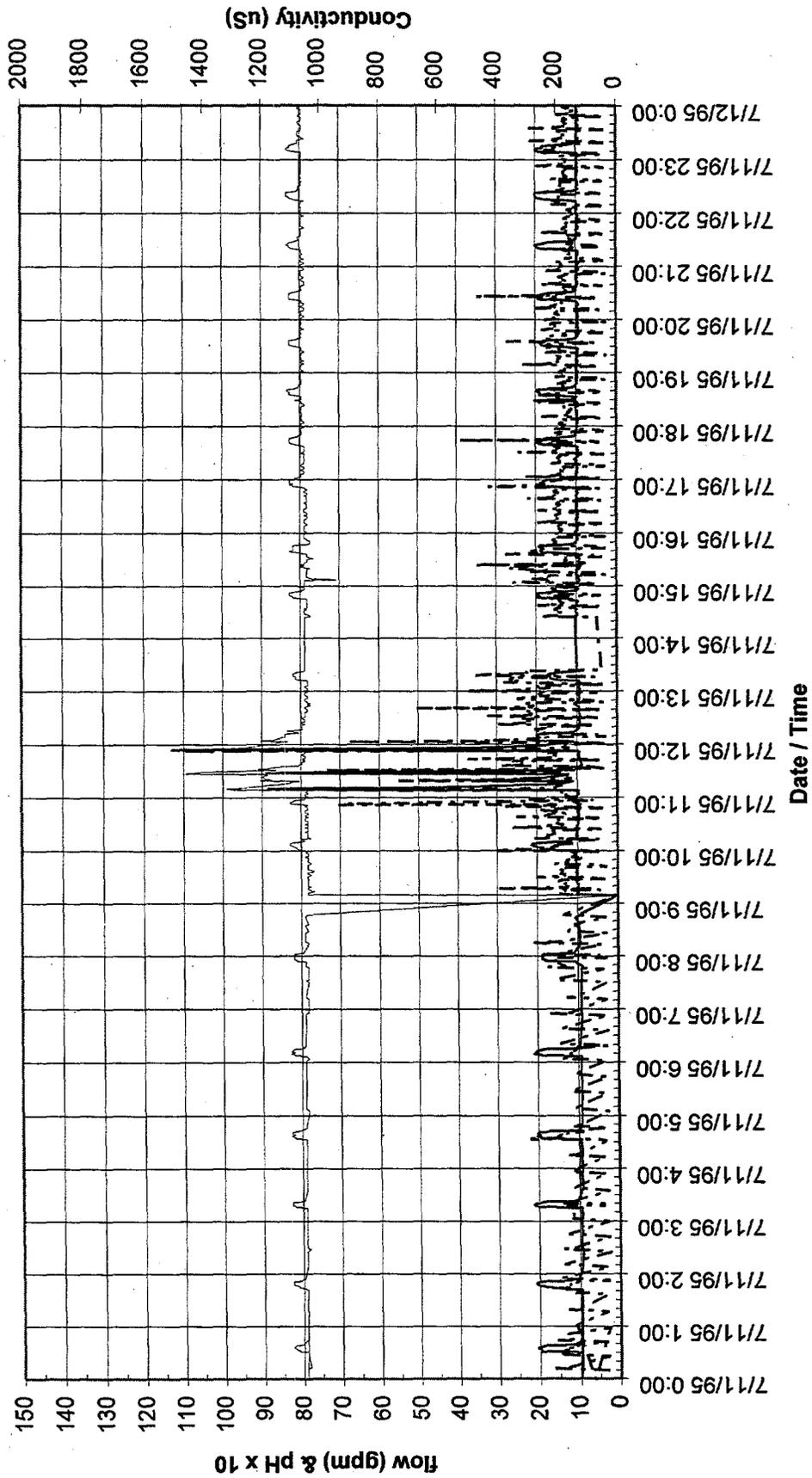
Appendix B

**Continuous Monitoring Data
July 11, 1995, through July 21, 1995**

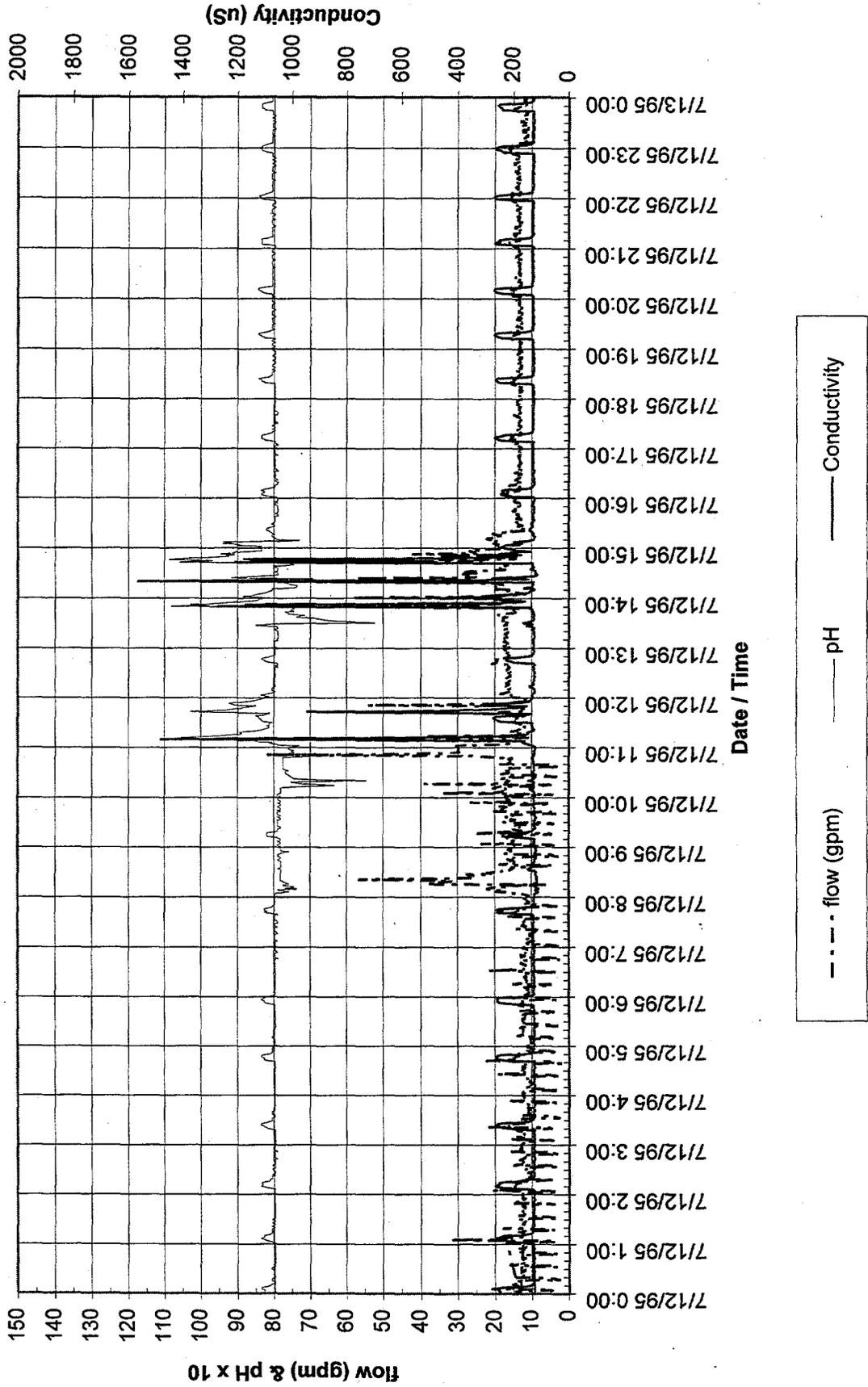
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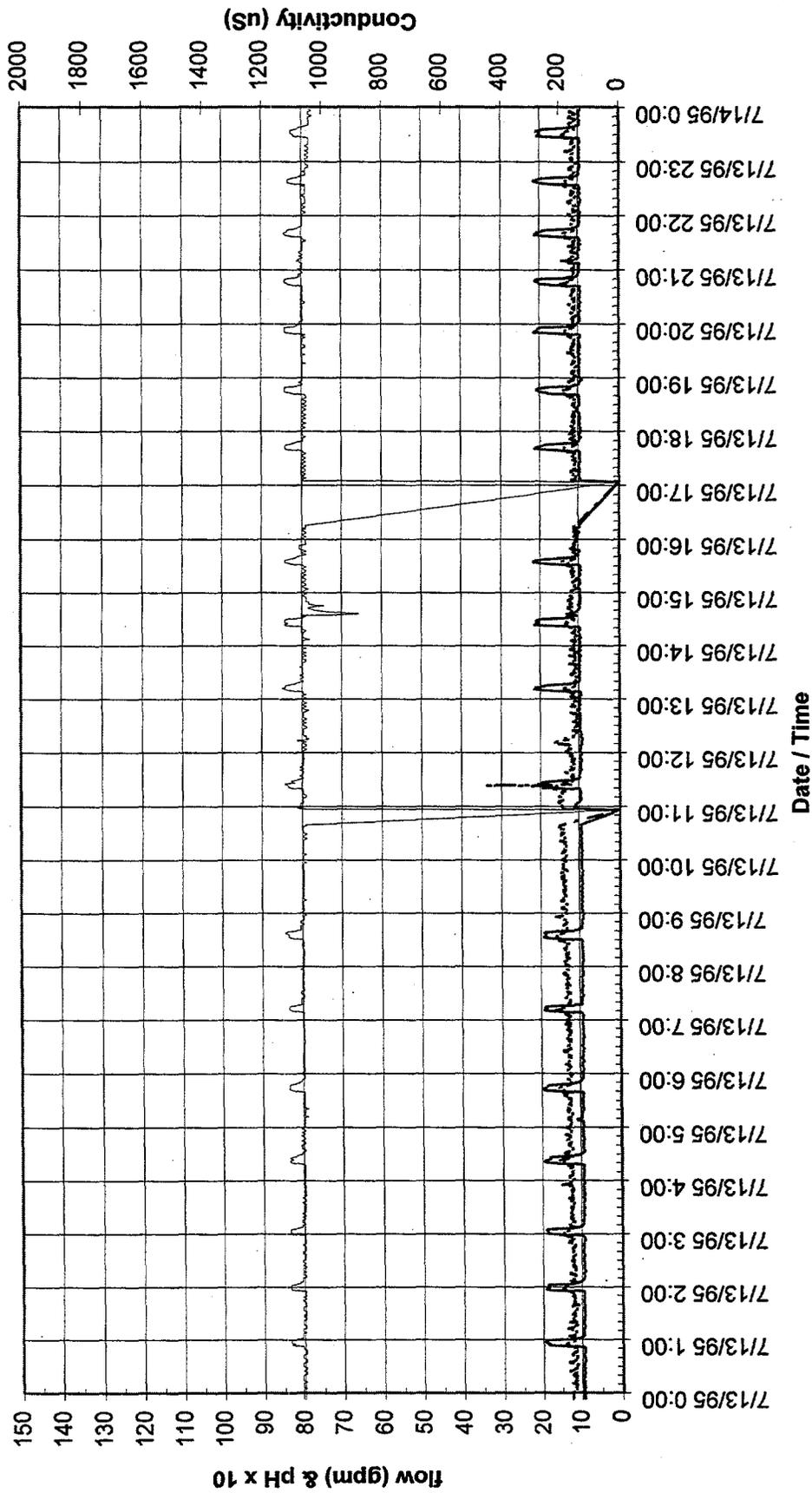
331 PS Data 11 Jul 95 (Tuesday)



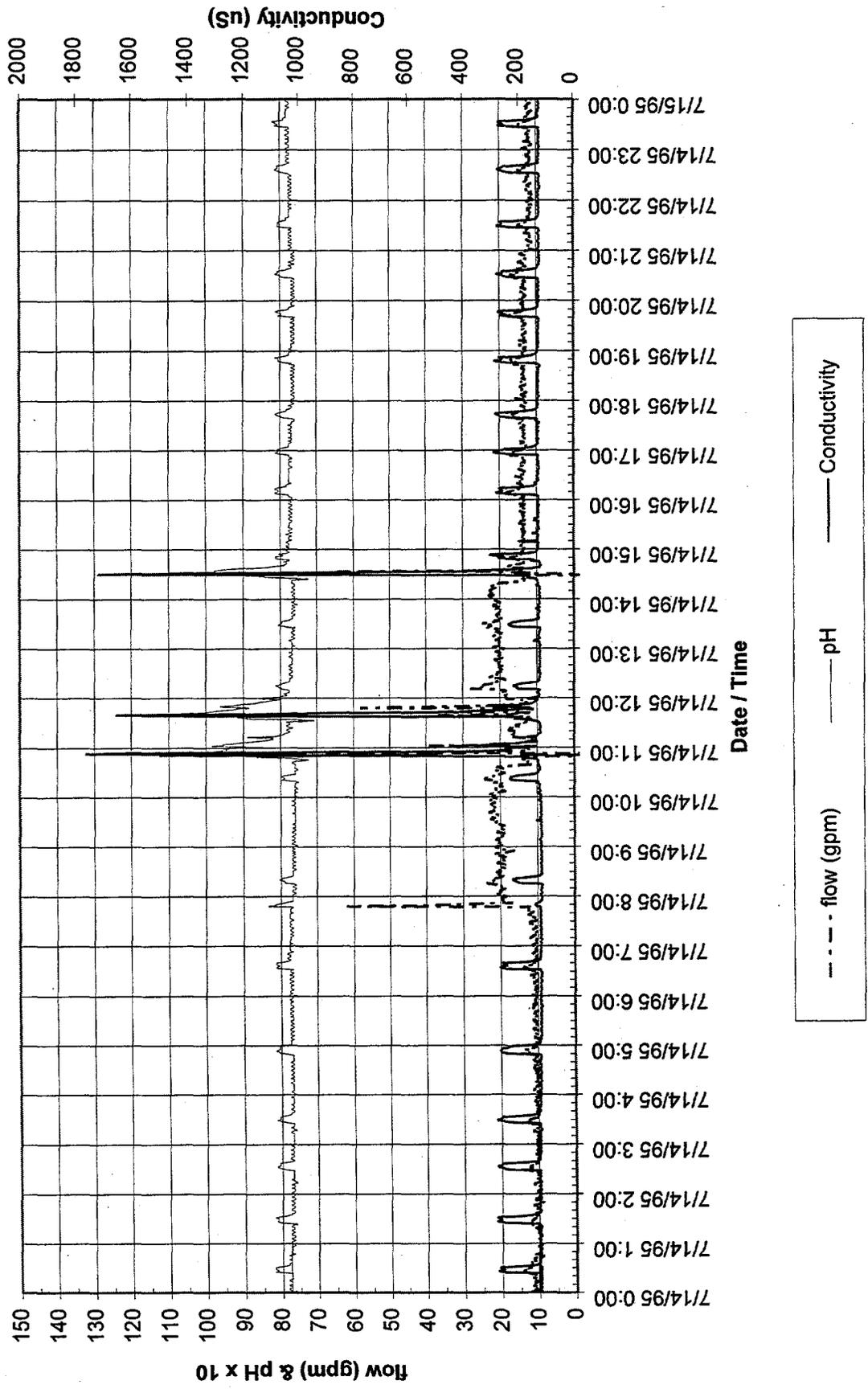
331 PS Data 12 July 95 (Wednesday)



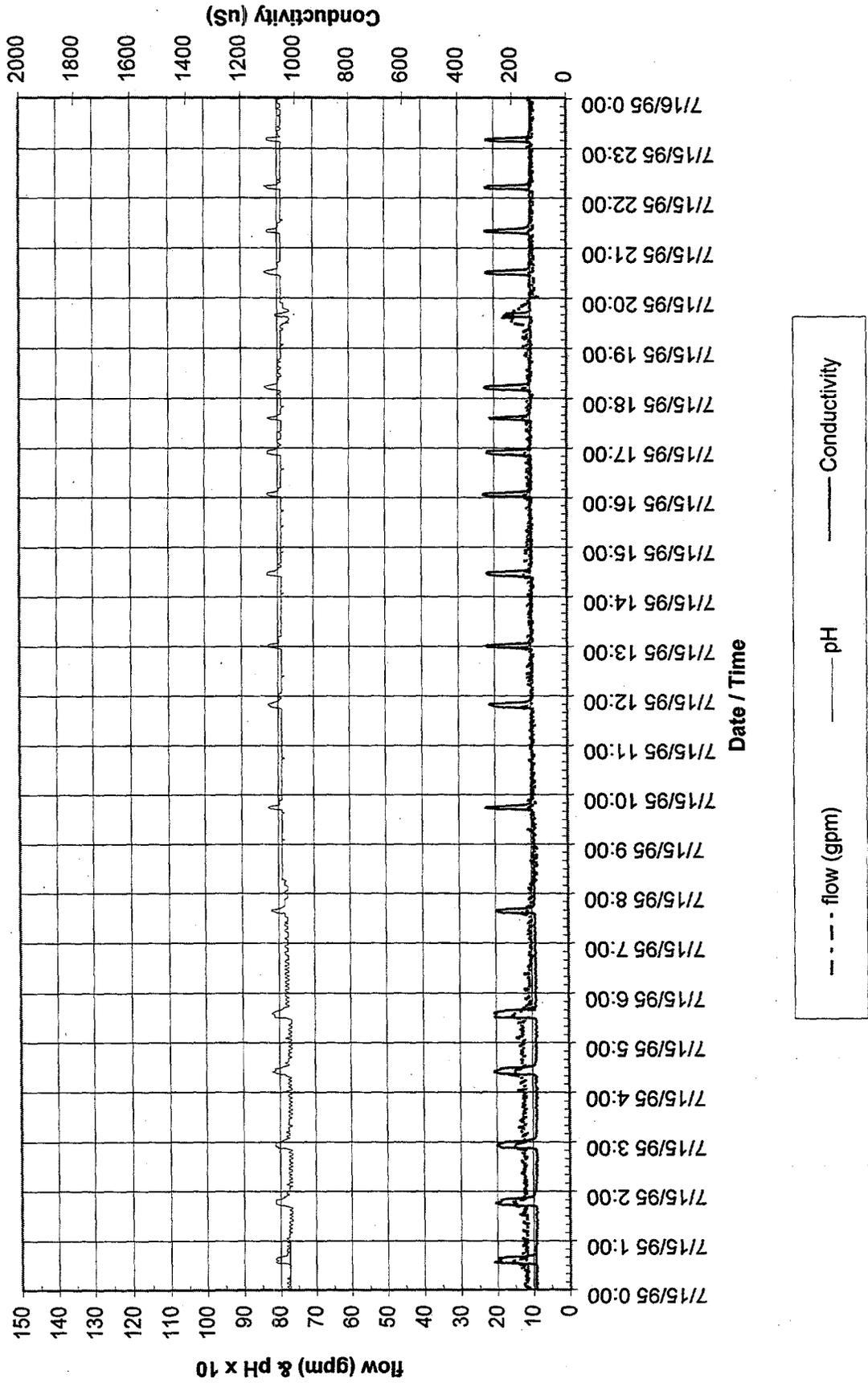
331 PS Data 13 July 95 (Thursday)



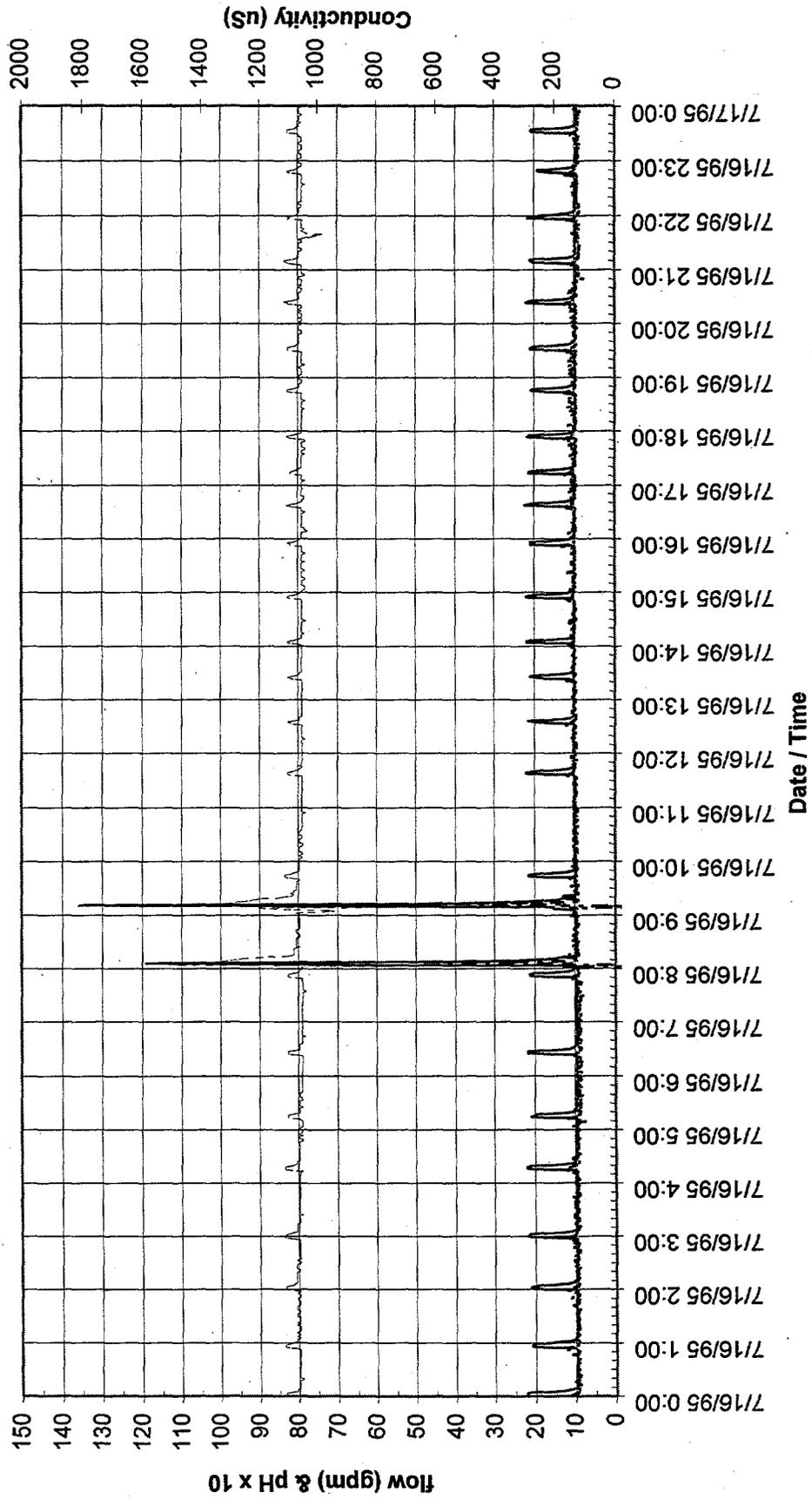
331 PS Data 14 July 95 (Friday)



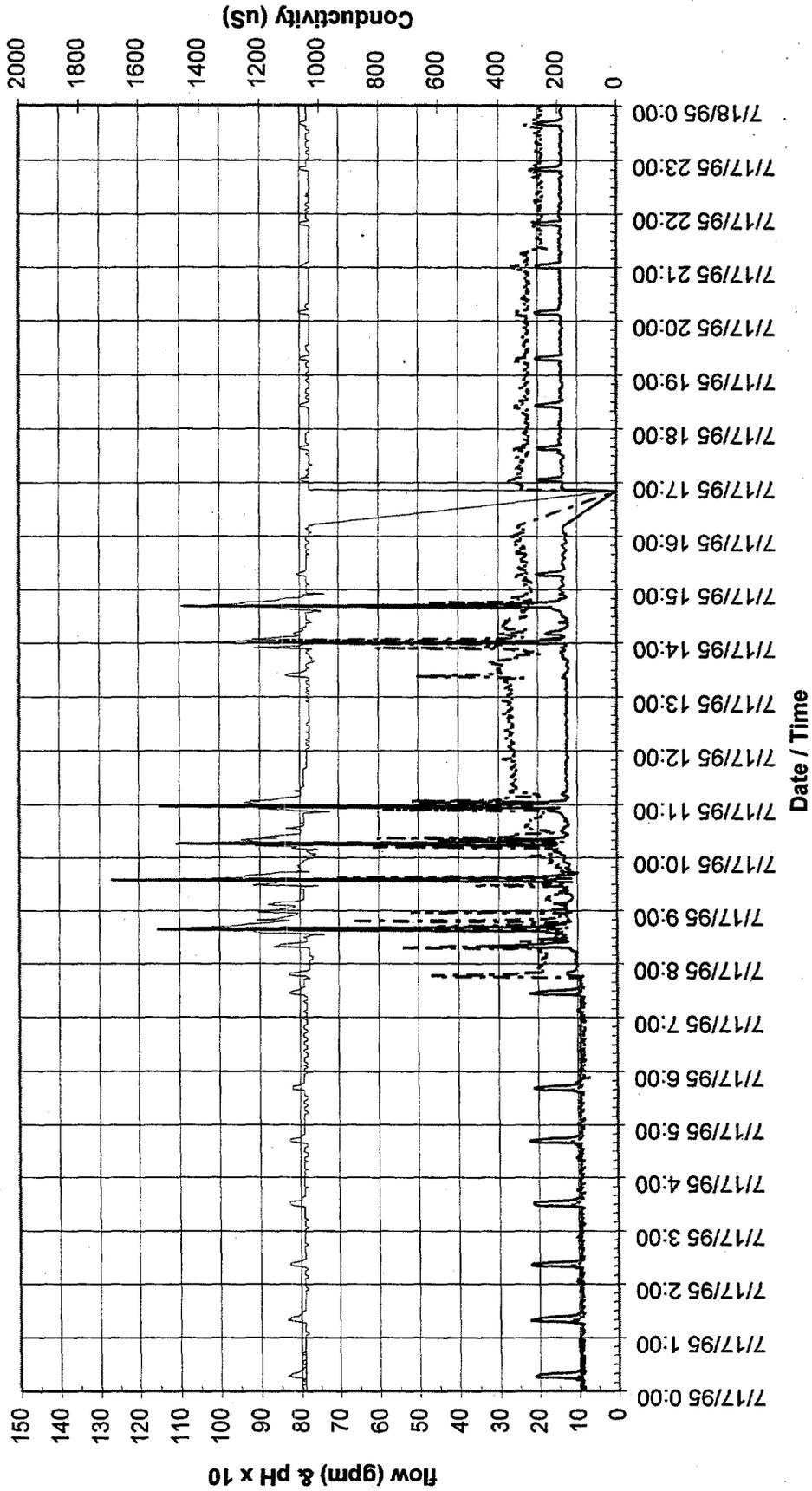
331 PS Data 15 July 95 (Saturday)



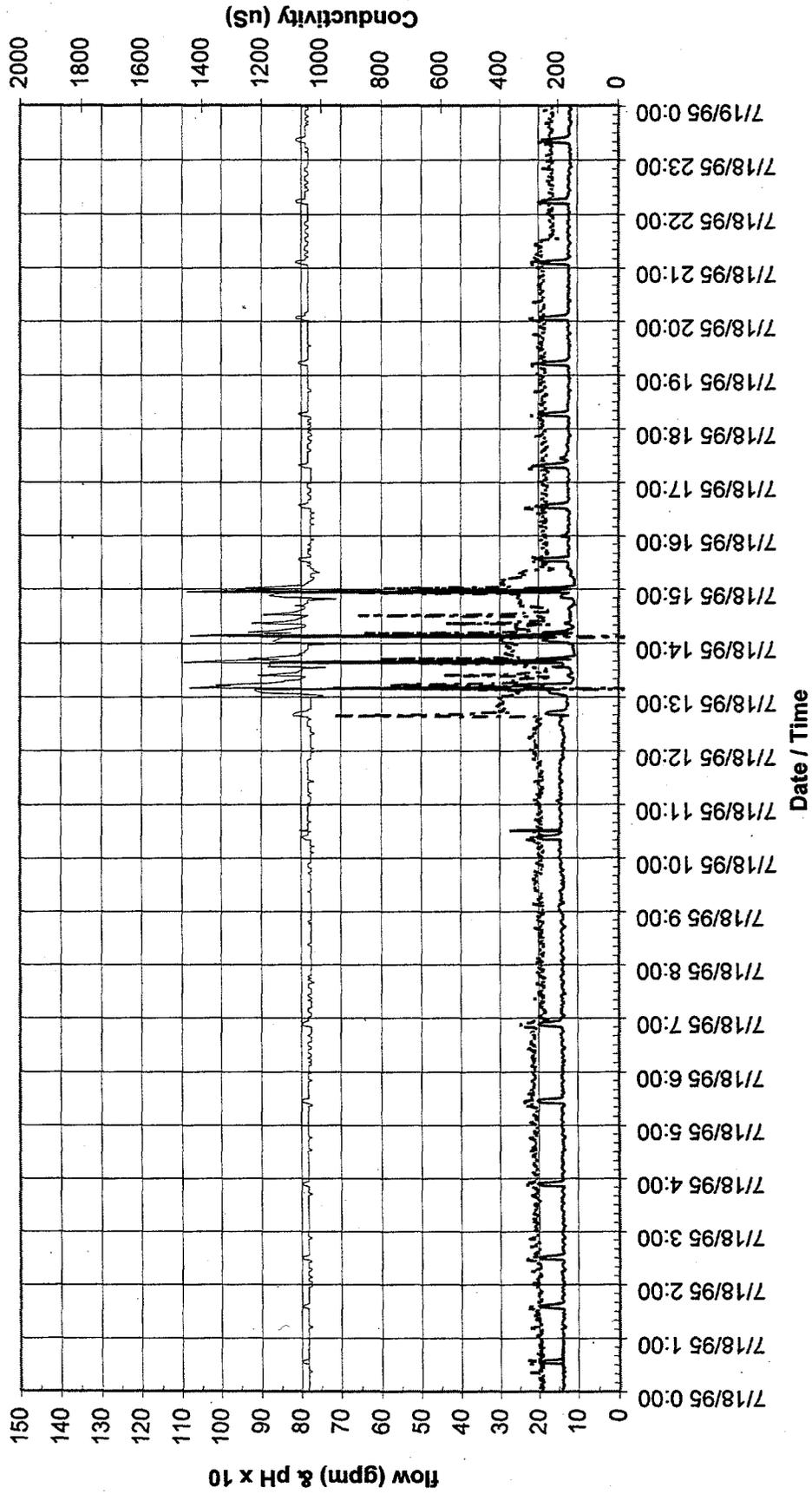
331 PS Data 16 July 95 (Sunday)



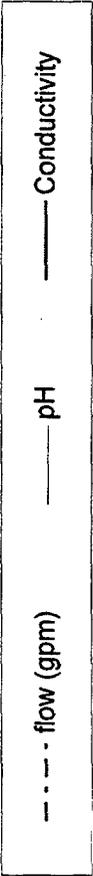
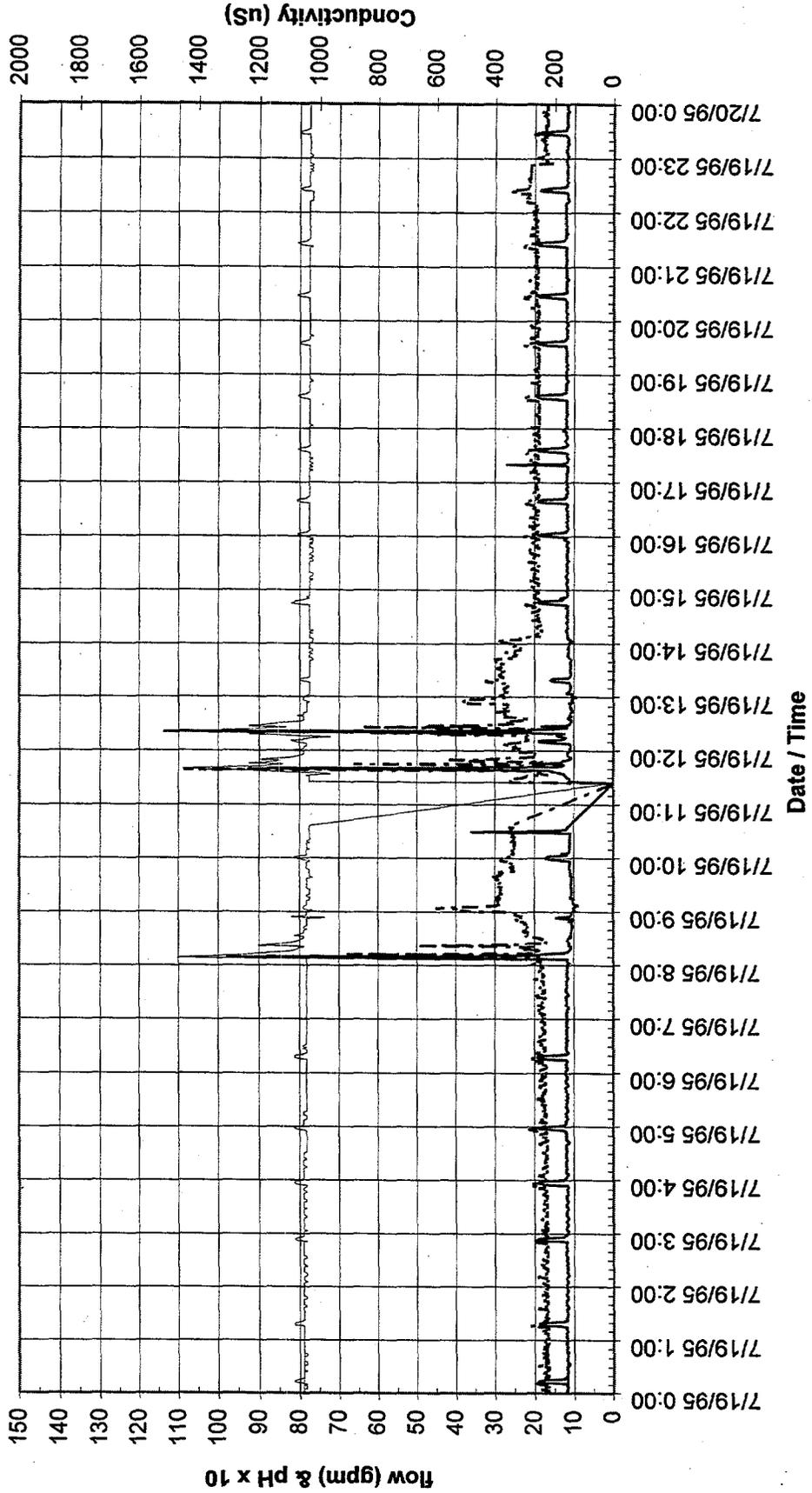
331 PS Data 17 July 95 (Monday)



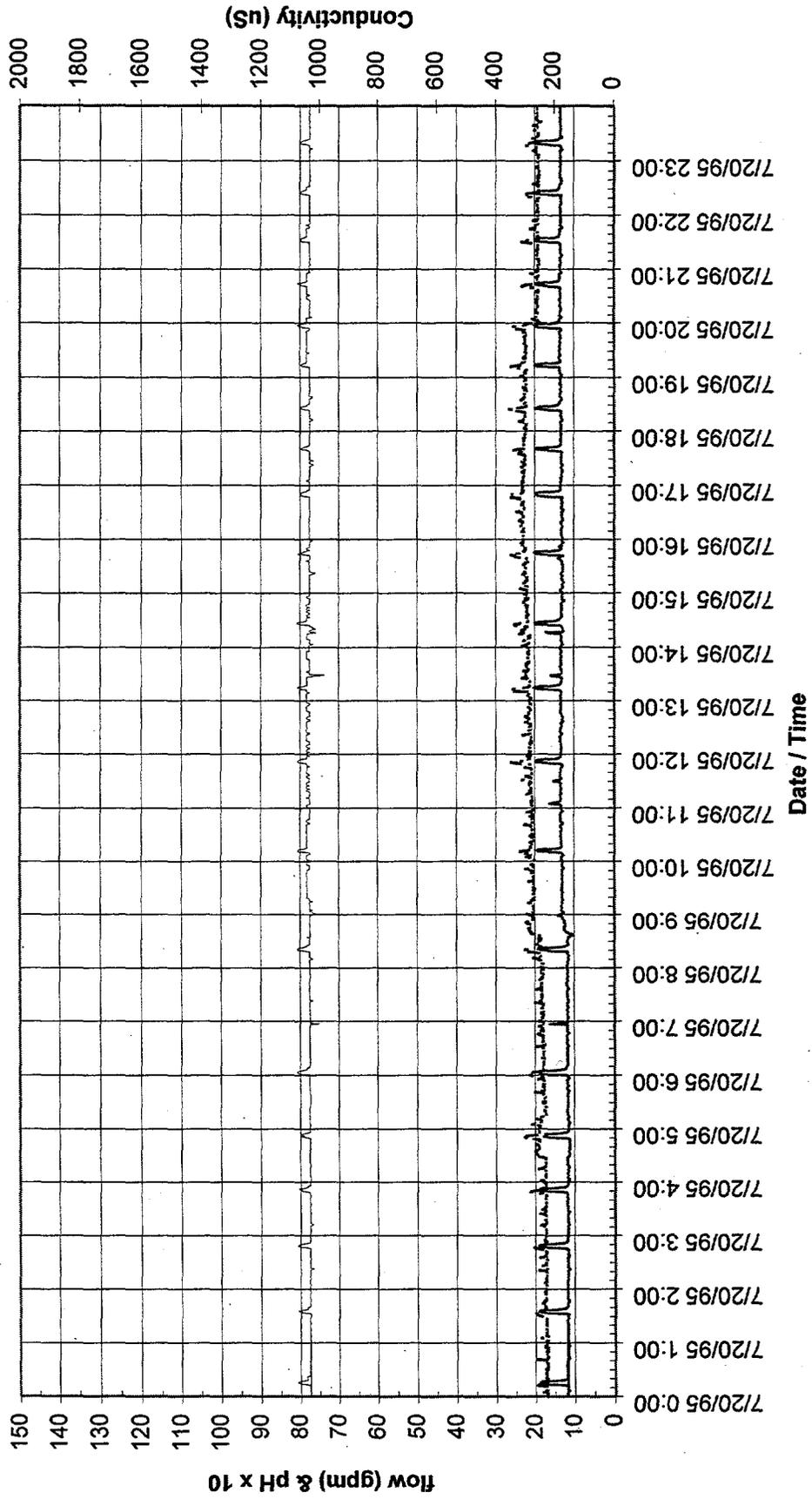
331 PS Data 18 July 95 (Tuesday)



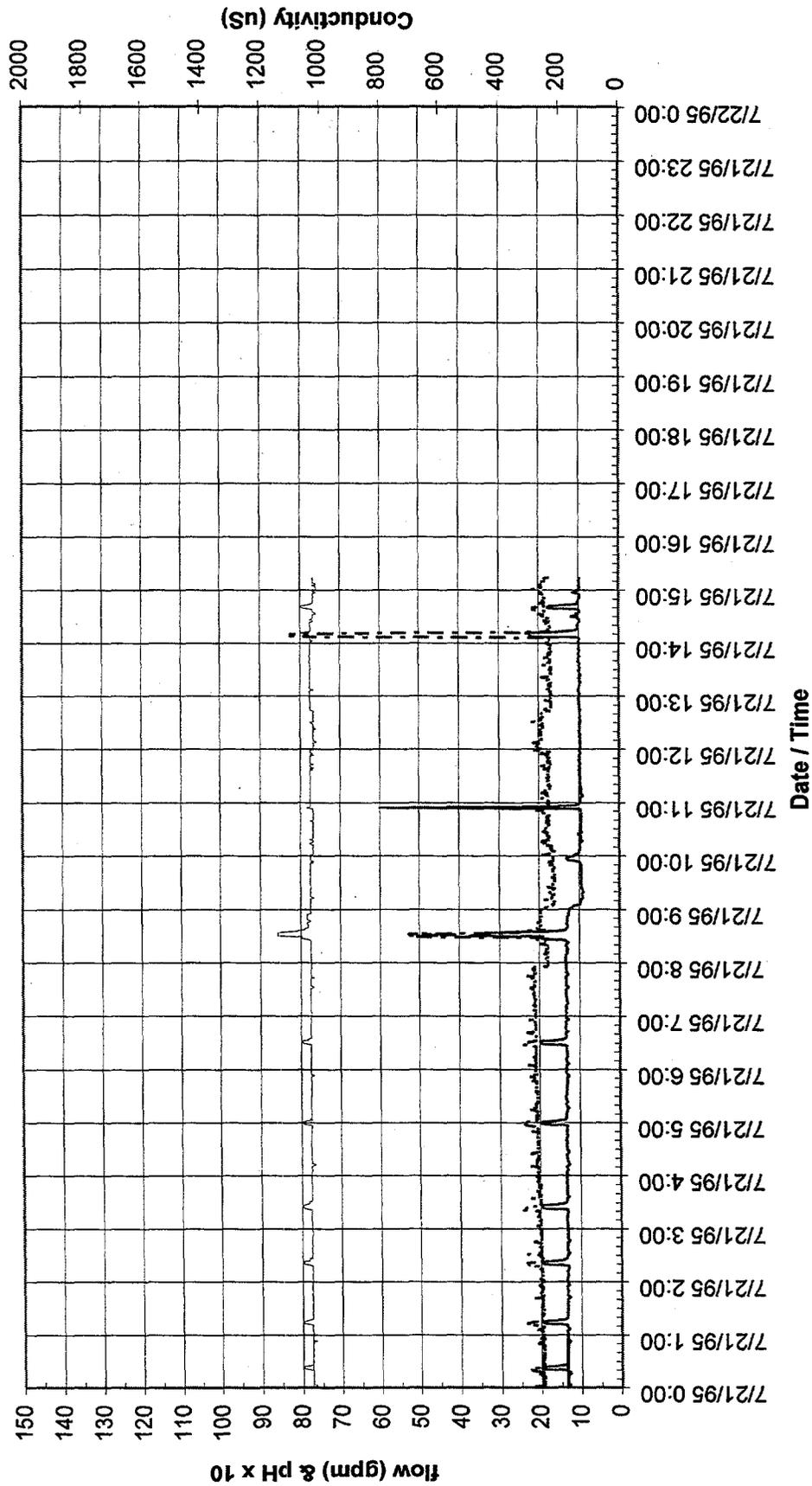
331 PS Data 19 July 95 (Wednesday)



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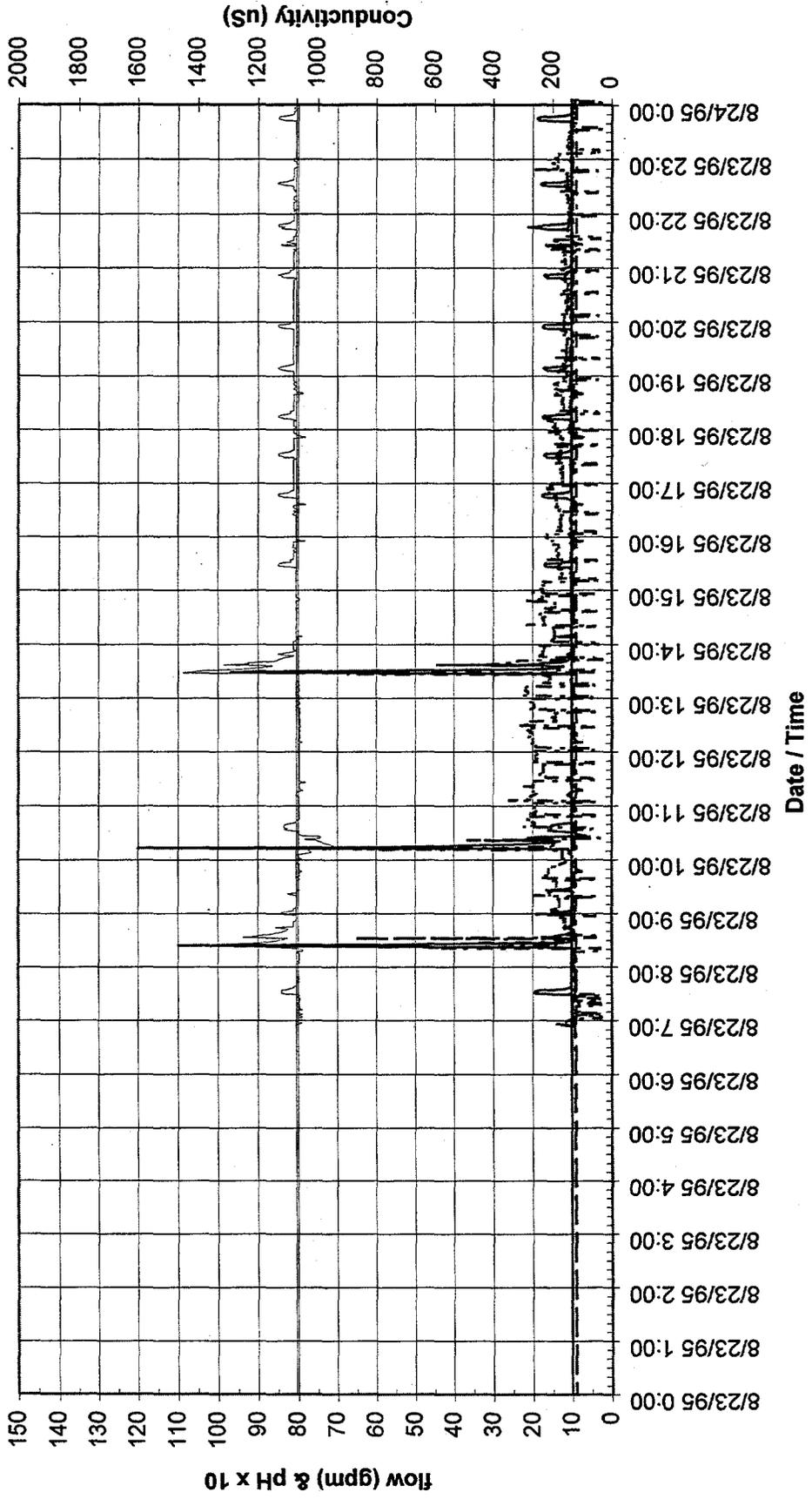
331 PS Data 21 July 95 (Friday)



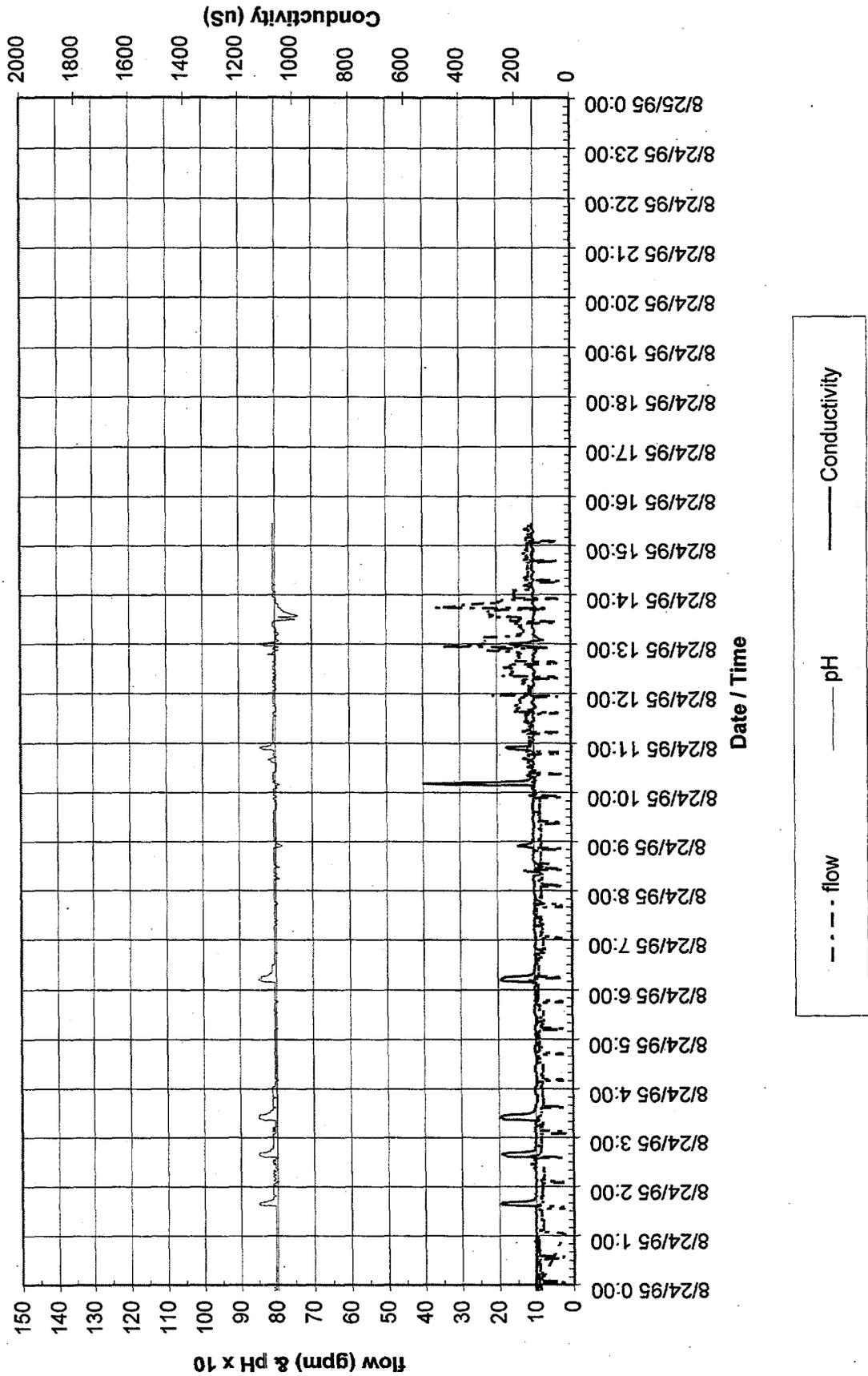
Appendix C

**Continuous Monitoring Data
August 23, 1995, through September 8, 1995
(Excluding August 25 through August 30)**

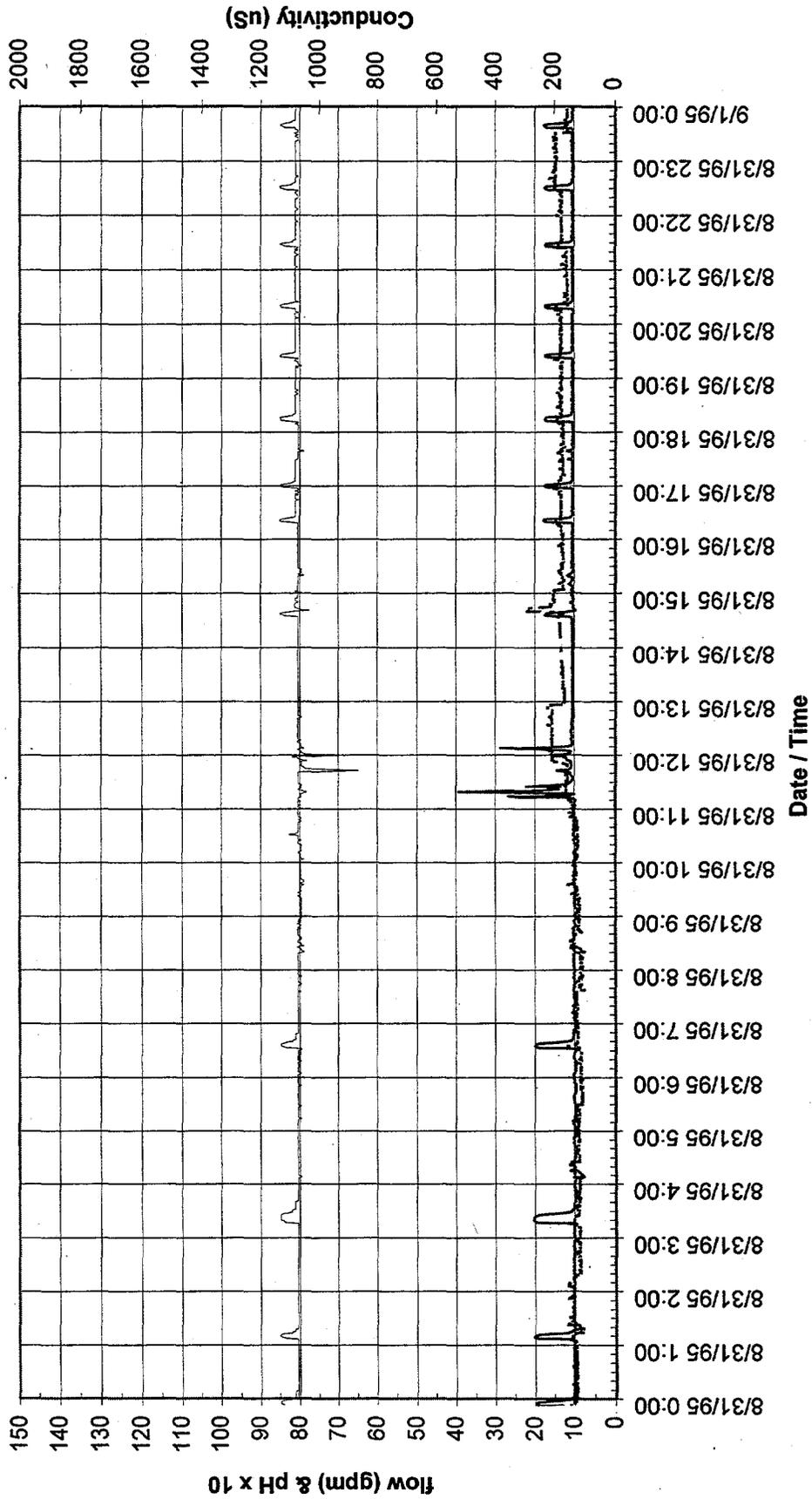
331 PS Data 23 Aug 95 (Wednesday)



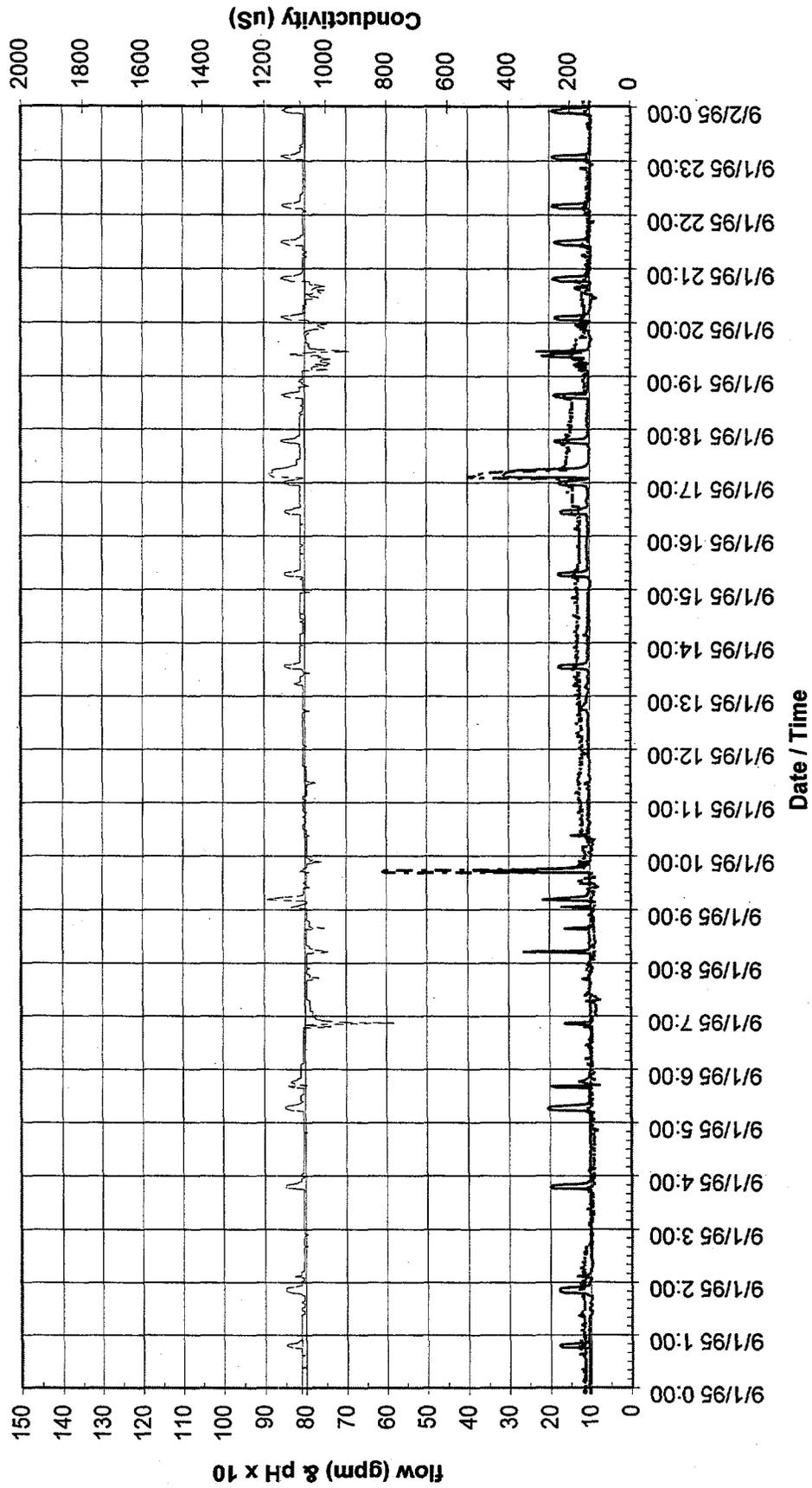
331 PS Data 24 Aug 95 (Thursday)



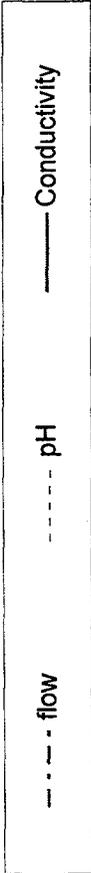
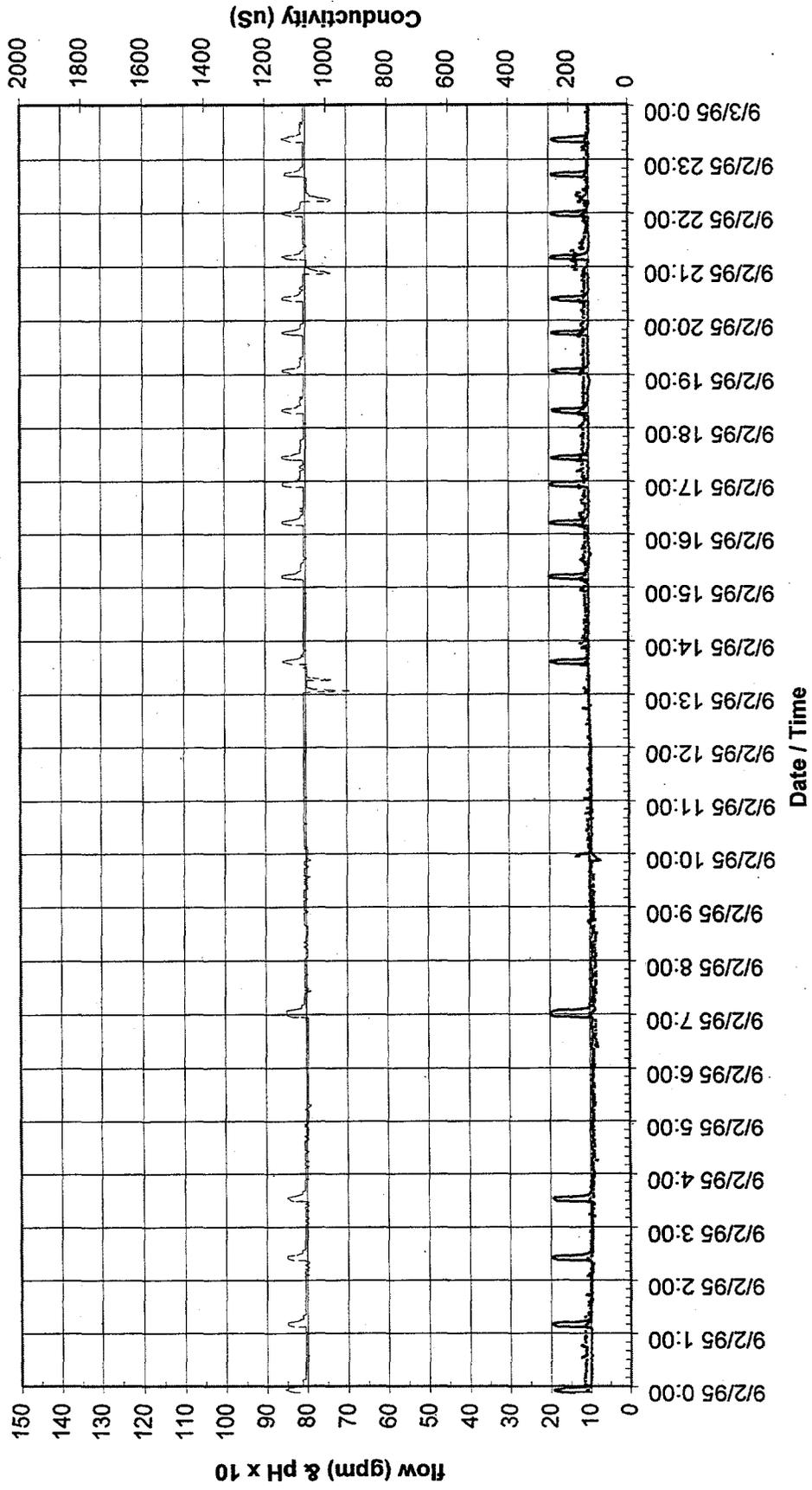
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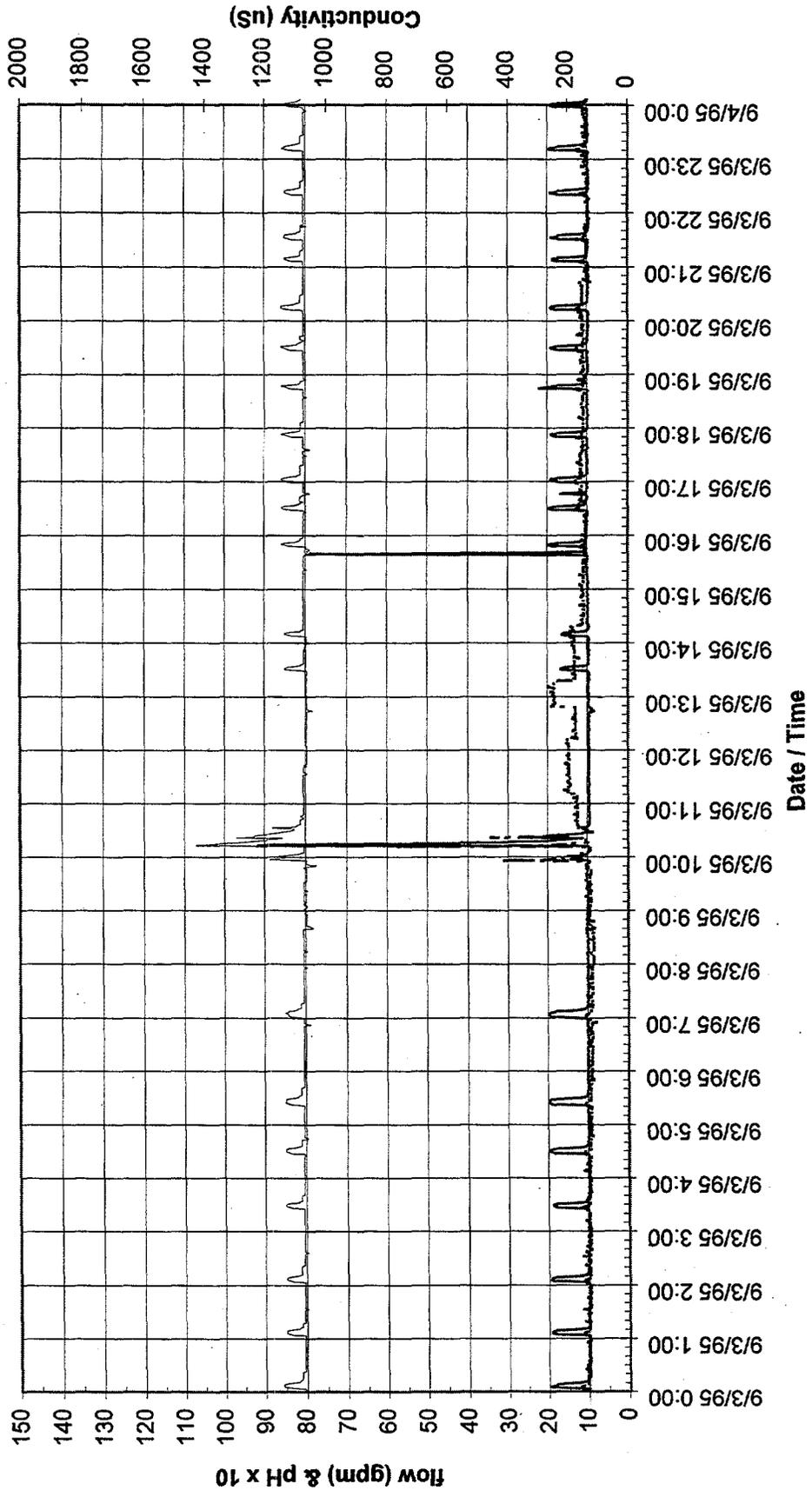
331 PS Data 1 Sept 95 (Friday)



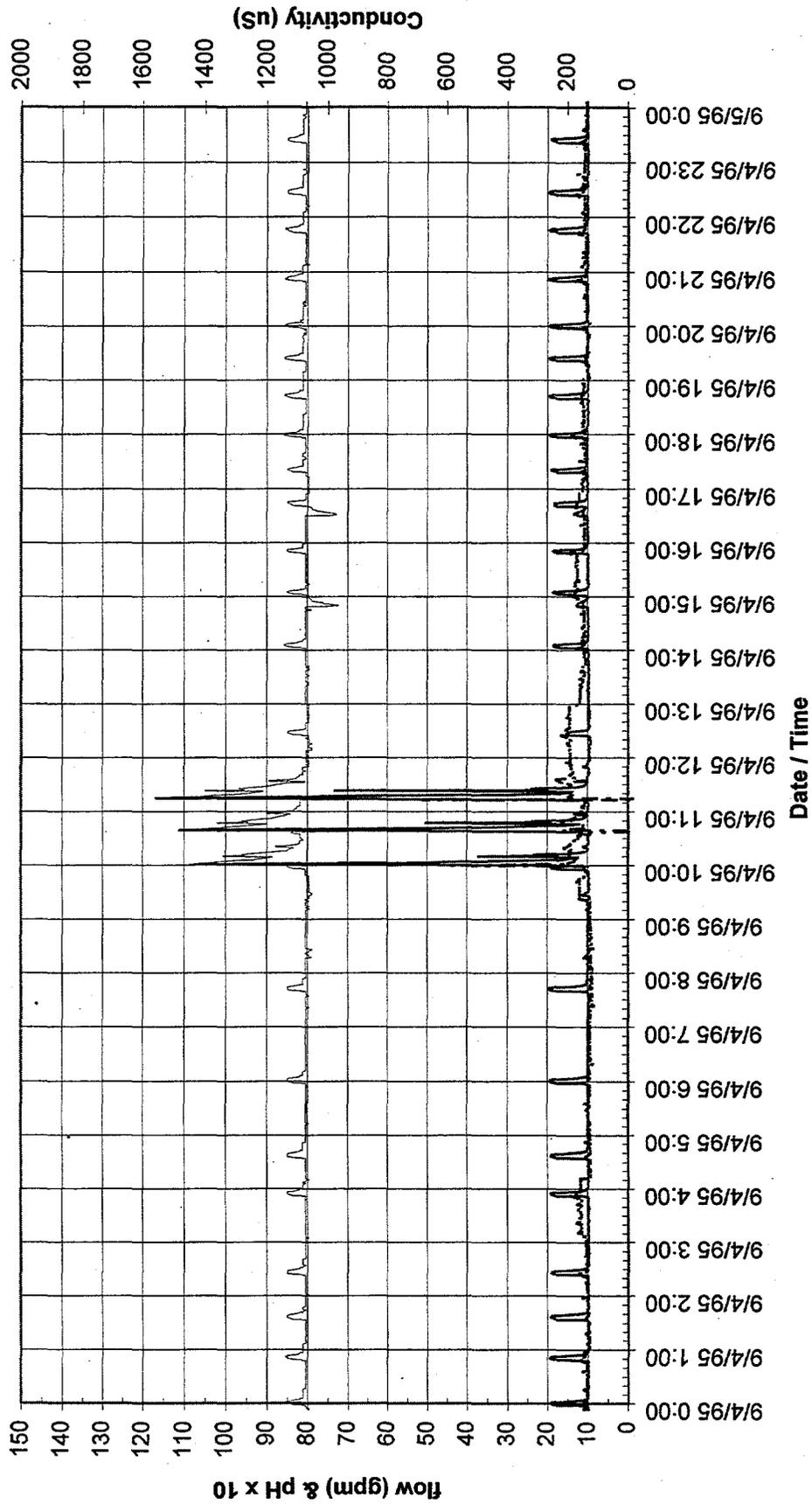
331 PS Data 2 Sept 95 (Saturday)



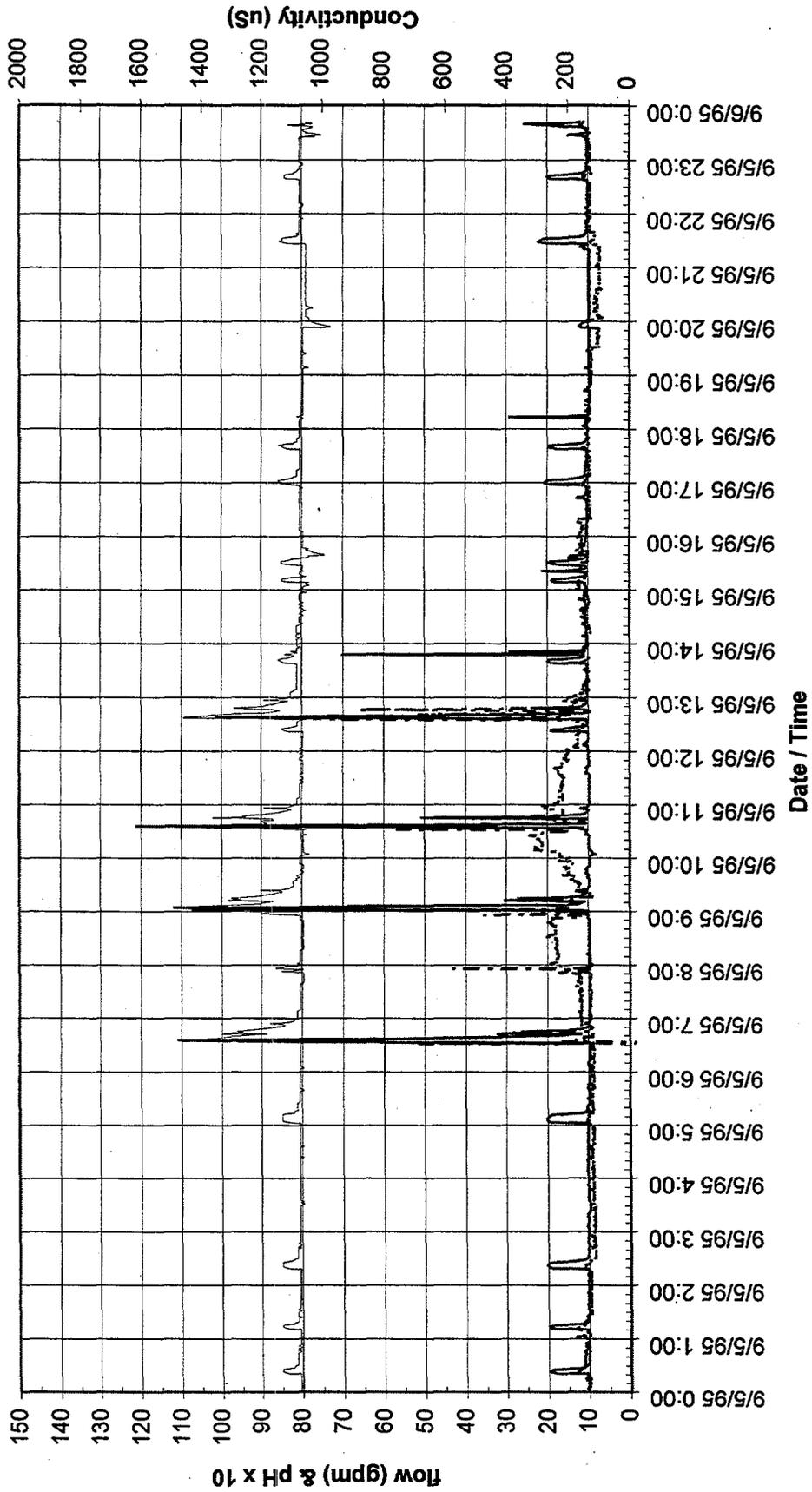
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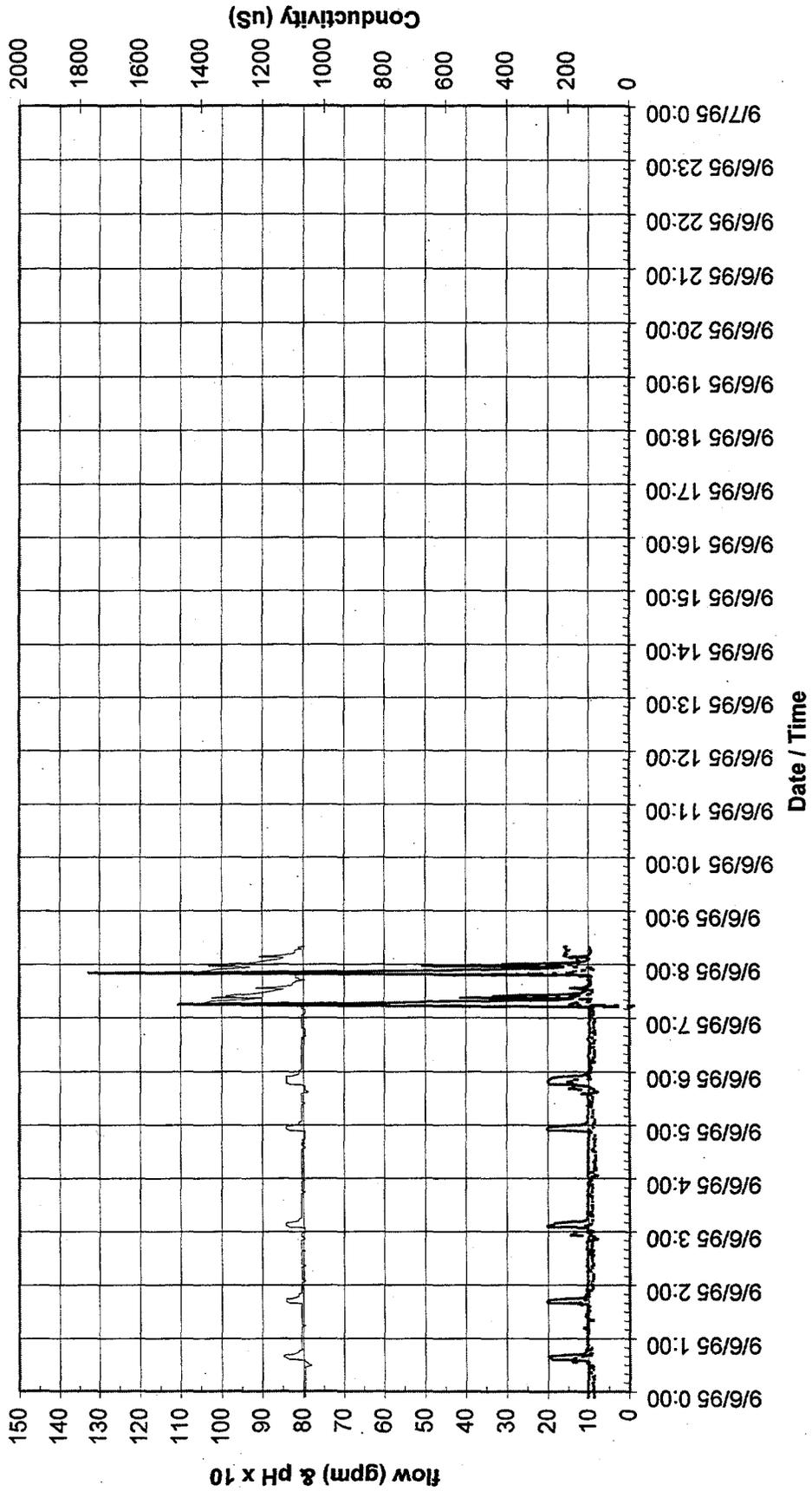
331 PS Data 4 Sept 95 (Monday)



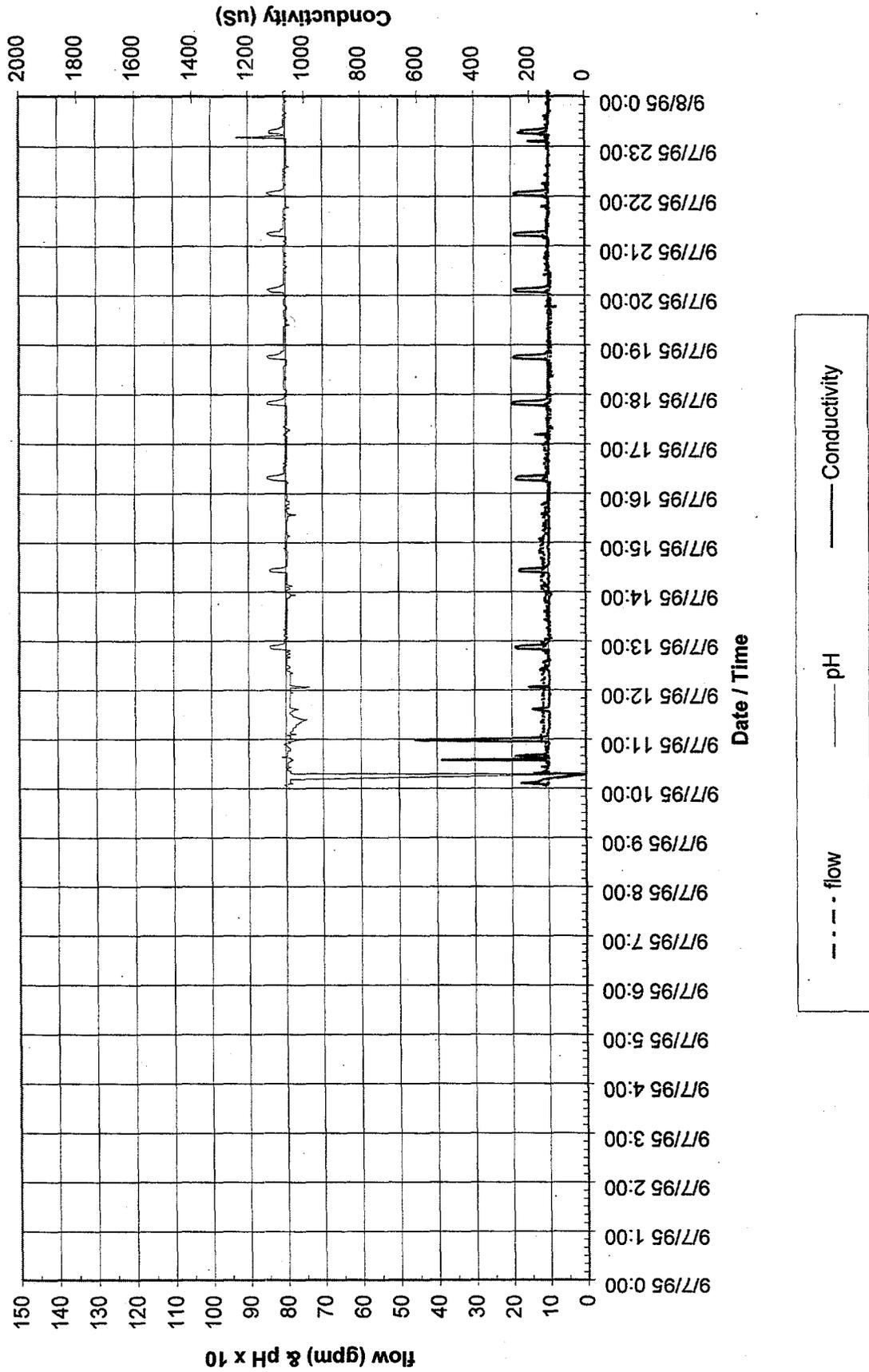
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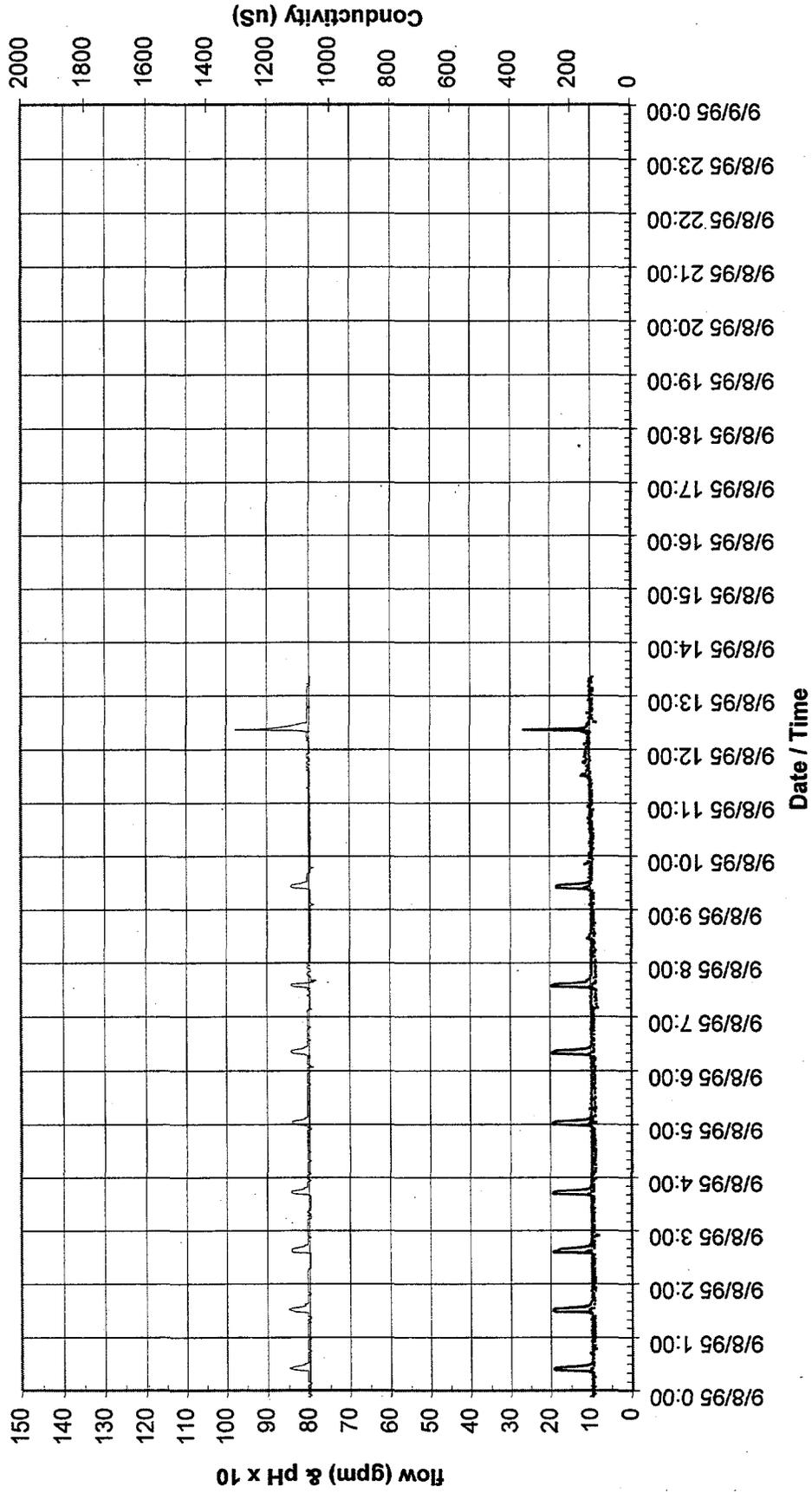
331 PS Data 6 Sept 95 (Wednesday)



331 PS Data 7 Sept 95 (Thursday)



331 PS Data 8 Sept 95 (Friday)



Appendix D

Data Set Summaries for Campaigns 1 and 2 Event-Triggered Sampling and Analysis

Table D.1. Campaign 1 Event-Triggered Sampling and Analysis Data^(a)

Date	Day	Sample Number	Trigger	Pattern	Time	pH	Peak pH	Cond	Peak Cond	Selected Anions and Metals								
										F	Cl	NO ₃	PO ₄	SO ₄	NO ₂	Cu	Zn	
Campaign 1																		
7/11/95	Tues	14	High pH, cond	1	11:08	7.83	10	134.2	1200	2.7	8.88	108.9	369.7	18	0.056	0.061	0.02	
7/11/95	Tues	15	High pH, cond	1	11:09	9.75	10	1118	1200	2.96	10.91	138.7	482.7	22.6	0.043	0.044	0.01	
7/11/95	Tues	16	High pH, cond	1	11:10	9.9	10	1182	1200	2	9.2	105.7	366.2	19.3	0.053	0.061	0.03	
7/11/95	Tues	17	High pH, cond	1	11:12	9.08	10	466.1	1200	1.79	2.58	53.3	166.3	20.9	0.119	0.037	0.1	
7/11/95	Tues	18	High pH	1	11:17	8.27	9	168.5	470	0.594	5.64	7.5	19.9	18.15	0.017	0.018	0.08	
7/11/95	Tues	19	High pH, cond	1	11:19	9.05	9	472.2	470	0.797	6.74	24.1	60.9	0.6	0.046	0.032	0.09	
7/11/95	Tues	20	High pH	1	11:20	8.79	9	277.1	470	0.707	6.54	27.6	71.6	18.5	0.059	0.018	0.1	
7/13/95	Thurs	3	High pH, cond	2	14:23	8.41	8.5	287.5	300	0.878	8.4	1.3	0.4	34.3	0.023	0.027	0.1	
7/13/95	Thurs	4	Low pH	2	14:35	6.93	6.5	174.8	200	2.39	10.06	0.8	1.8	15.8	0.05	0.009	0.23	
7/13/95	Thurs	5	High pH, cond	2	15:34	8.42	8.5	287.7	300	0.754	7.96	1.2	0.4	33.4	0.033	0.029	0.08	
7/14/95	Fri	1	High pH, cond	1	10:44	7.46	8.5	131.9	1500	0.573	4.38	3.2	26.9	23.1	0.026	0.138	0.11	
7/14/95	Fri	2	High pH, cond	1	10:54	9.91	11	384.3	1800	0.858	10.9	17.3	59.2	22.4	0	0.037	0.22	
7/14/95	Fri	3	High pH, cond	1	11:42	10.5	11	847.4	1650	0.743	8.7	12.1	41.4	22.3	0.023	0.02	0.48	
7/14/95	Fri	4	High pH	1	11:04	9.31	9.8	241.2	380	0.626	6.33	5.7	18.5	21.4	0.05	0.034	0.22	
7/18/95	Tues	3	High pH, cond	1	13:11	10.13	10.8	395	1000	0.892	16.3	21.5	37.5	22.9	0.026	0.018	0.06	
7/18/95	Tues	7	Low pH	1	13:58	7.46	6.9	151.4	160	0.445	7.16	5.4	9	19.8	0.023	0.049	0.08	
7/18/95	Tues	8	High pH, cond	1	14:08	10.19	10.8	445.5	1300	1.03	13.4	23.2	74.7	20	0.013	0.041	0.08	
7/18/95	Tues	10	High pH	1	14:32	8.94	9	162.3	180	0.547	6.86	1.5	0.5	18.4	0.02	0.028	0.18	
7/18/95	Tues	11	Low pH	1	14:48	7.45	7.1	148.3	160	0.565	7.25	5.8	11.4	19.2	0.026	0.056	0.1	
7/18/95	Tues	12	High pH, cond	1	14:58	9.76	11	312.3	1400	0.738	10.4	15	28.2	19.3	0.023	0.009	0.04	
7/19/95	Wed	15	Low pH	2	8:52	7.41	7.4	189.4	200	0.423	6.24	2.7	1.9	34.8	0.026	0.138	0.15	
7/19/95	Wed	16	cond	2	10:28	7.77	7.8	272	500	0.788	63.4	2.5	0.3	19	0.033	0.664	0.21	

Table D.1. (contd)

Date	Day	Sample Number	Trigger	Pattern	Time	pH	Peak pH	Cond	Peak Cond	Selected Anions and Metals							
										F	Cl	NO3	PO4	SO4	NO2	Cu	Zn
7/19/95	Wed	1	Low pH	1	11:34	7.24	7.2	166.6	200	0.652	7.28	8.2	16.5	20.3	0.02	0.087	0.11
7/19/95	Wed	4	High pH	1	12:24	9.16	10.5	204.3	1550	0.777	8.32	9.5	16.8	19.8	0.026	0.017	0.08
7/19/95	Wed	5	cond	2	17:19	7.68	7.7	283.3	380	0.652	57	3.2	2.6	20.1	0.05	0.325	0.11
7/20/95	Thurs	6	Low pH	2	13:27	7.52	7.4	219.3	220	4.11	36.9	4.8	0.6	21	0.033	0.004	0.12
7/20/95	Thurs	7	cond	2	14:15	7.6	8	286.3	290	0.848	59.1	4.6	0.3	20.5	0.026	0.043	0.11
7/21/95	Fri	8	High pH, cond	2	8:29	8.05	8.5	293.4	500	1.72	25.8	3.9	1.5	72.3	0.053	0.152	1.6
7/21/95	Fri	9	cond	2	10:53	7.68	7.7	265.9	800	1.13	69.6	30.4	0.1	0.13	0.05	0.045	0.24
7/21/95	Fri	10	cond	2	14:09	7.9	8	297.5	300	0.604	12.8	15.6	0.3	31.4	0.083	0.025	0.11

(a) Conductivity is measured in microseverts (μS). Anion and metal concentrations are in parts per million (ppm).

Table D.2. (contd)

Date	Day	Sample Number	Trigger	Pattern	Time	pH	Peak pH	Cond	Peak Cond	Selected Anions and Metals							
										F	Cl	NO3	PO4	SO4	NO2	Cu	Zn
9/5/95	Tues	19	Low pH	2	19:53	7.45	7.3	156.9	180	0.335	6.59	6.7	0.2	18.2			
9/5/95	Tues	22	cond	2	23:39	8.12	8.4	291.2	360	7.78	22.8	0.2	25.9	40.4	0.45	0.24	
9/7/95	Thurs	2	cond	2	10:57	7.89	8	285.9	600	0.675	63.9	2.2	7.3	17.1			
9/7/95	Thurs	3	Low pH	2	12:03	7.45	7.4	203.7	200	0.591	6.54	32.3	1.3	17.1	0.2	0.19	
9/7/95	Thurs	6	High pH	2	16:16	8.34	8.5	245.1	200	0.317	3.2	1	0.3	16.3			
9/7/95	Thurs	12	High pH	2	23:10	8.26	9.3	126.8	200	0.568	6.89	1.7	0.2	37.3			
9/8/95	Fri	21	High pH, cond	2	12:21	8.35	9.8	151.4	380	0.944	3.65	1.5	1.2	23.4			

(a) Conductivity is measured in microseverts (μS). Anion and metal concentrations are in parts per million (ppm).

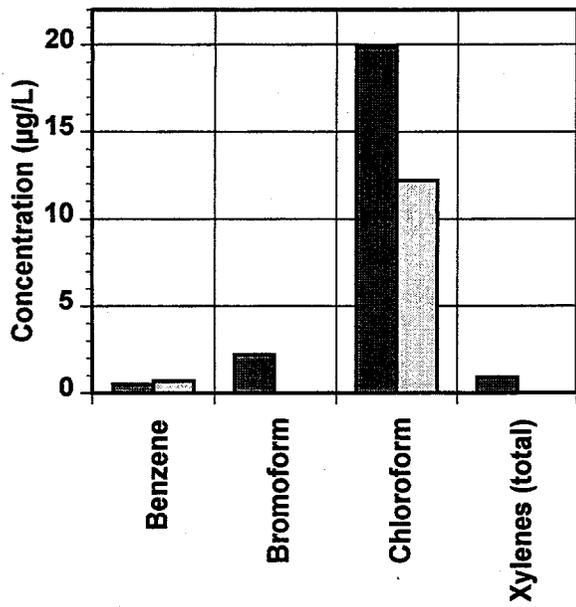
Appendix E

Summary of Off-Site Metals Analyses Performed on Event-Triggered Samples Collected During Campaign 2

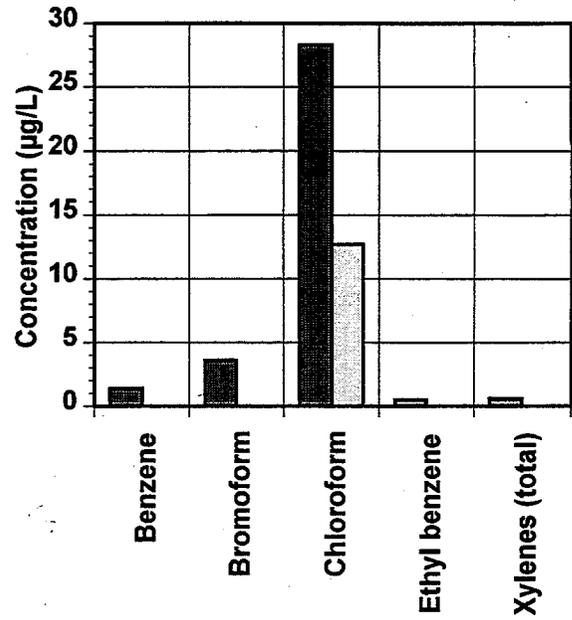
Appendix F

Summary of Concentrations in Volatile Organic Compound Hold-Time Study Samples

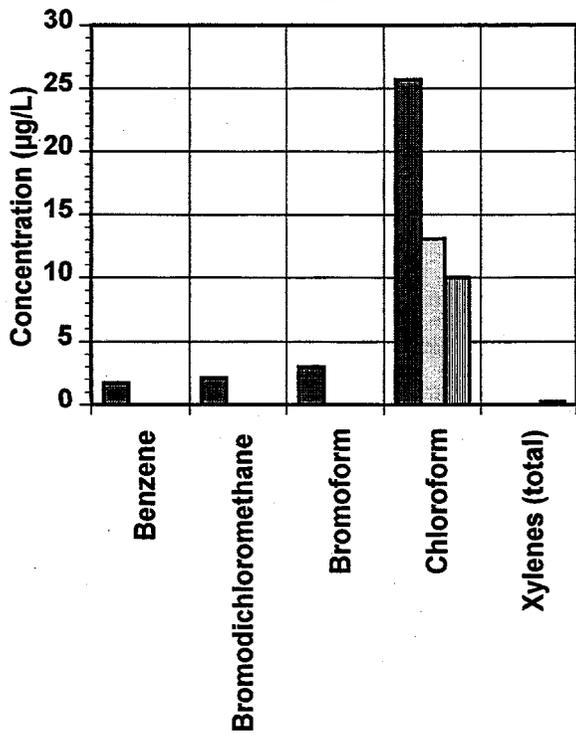
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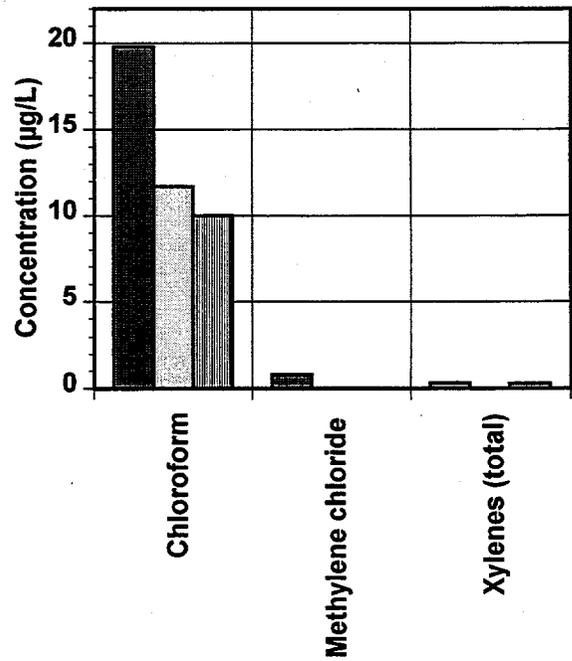
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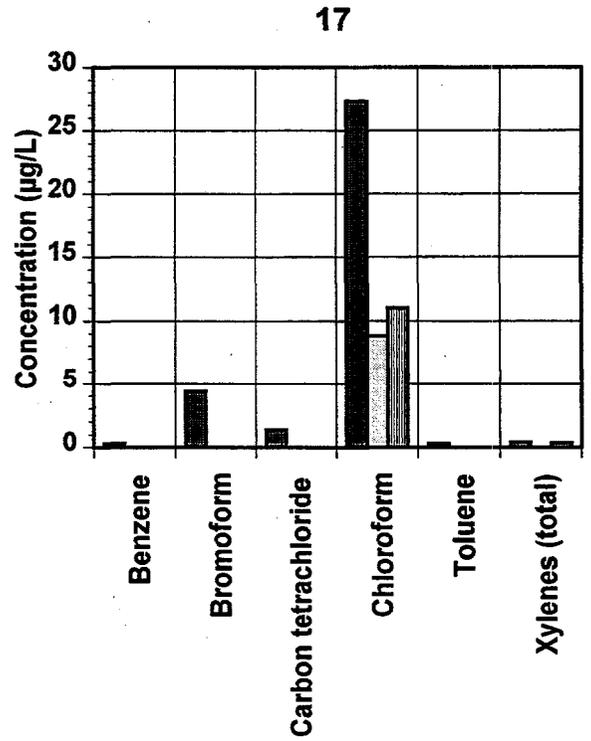
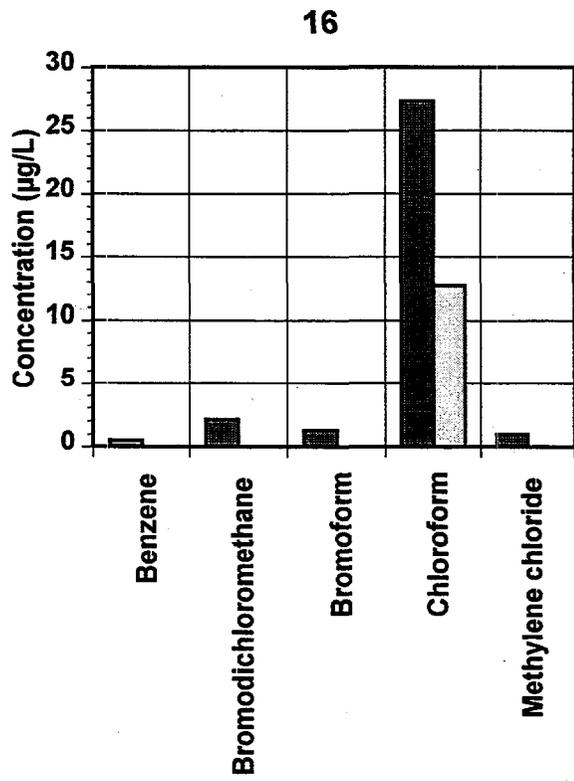
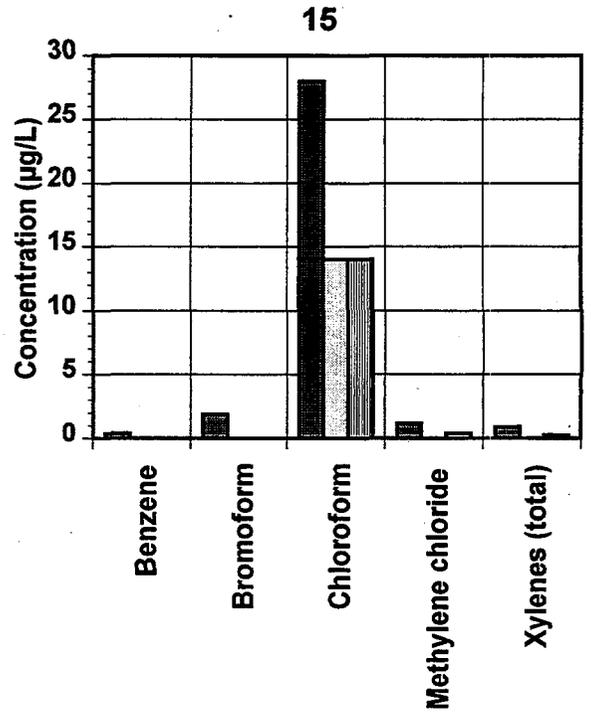
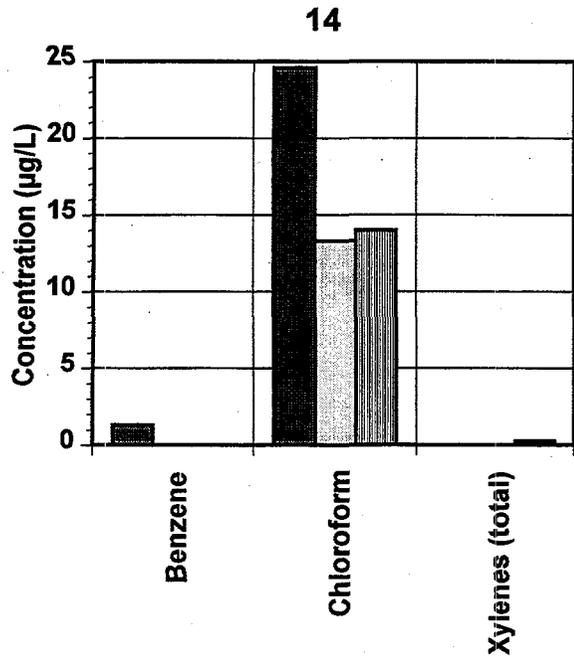


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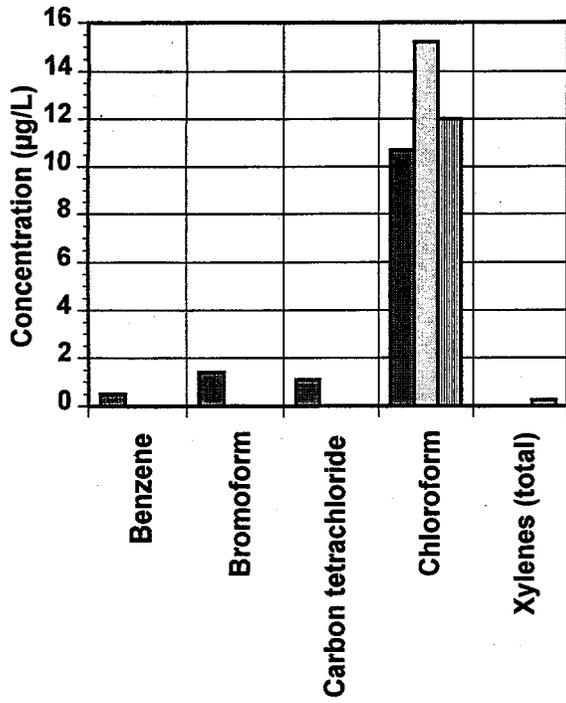


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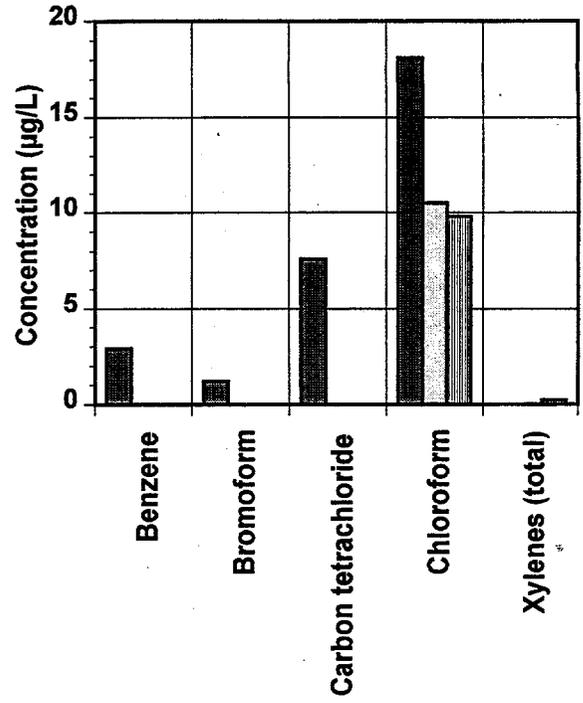




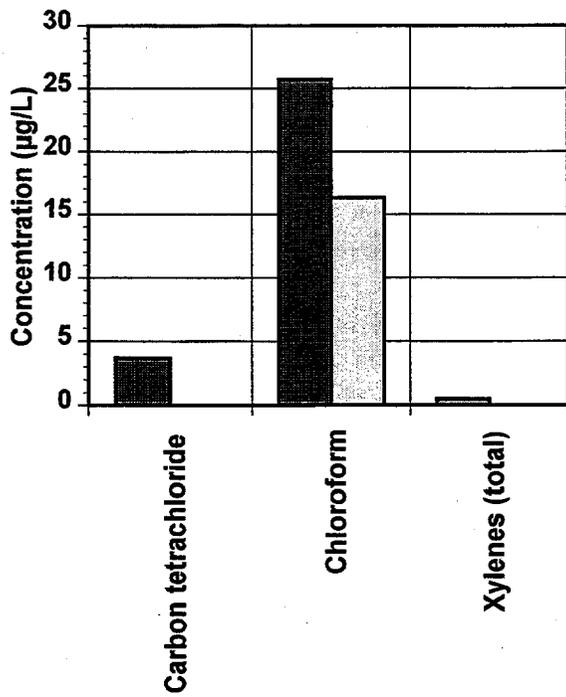
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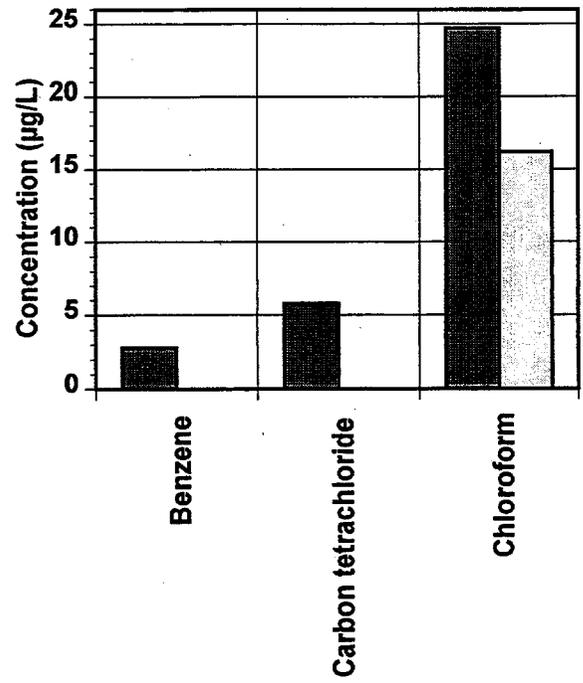
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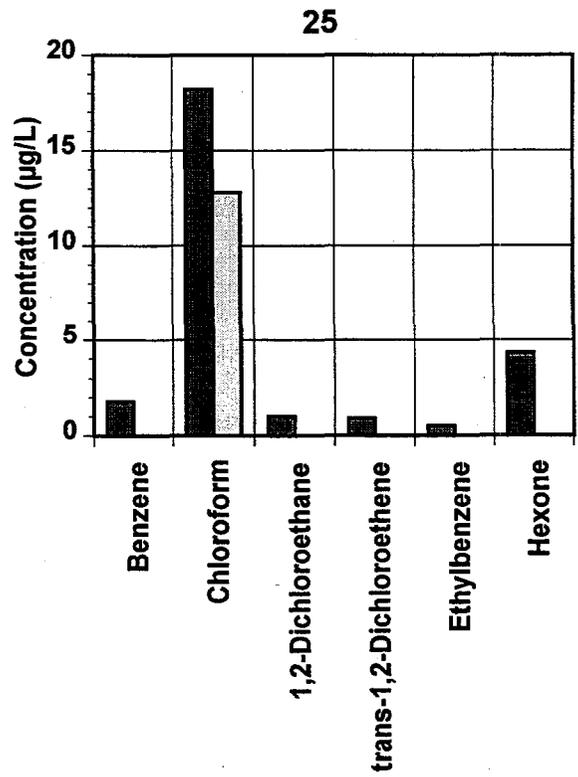
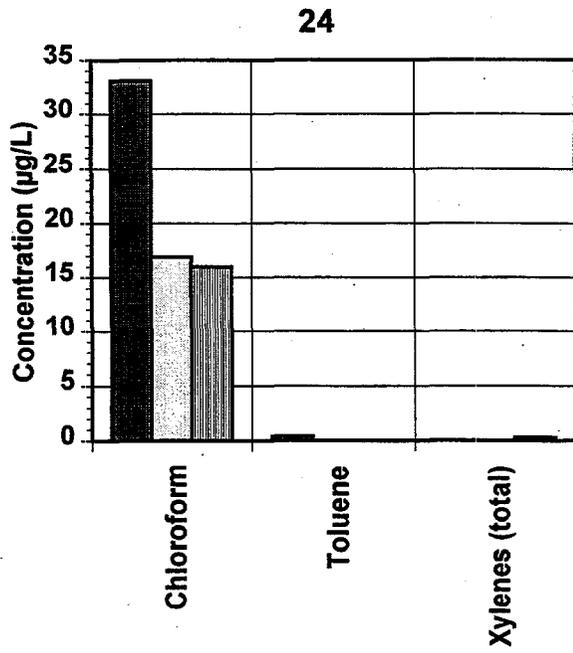
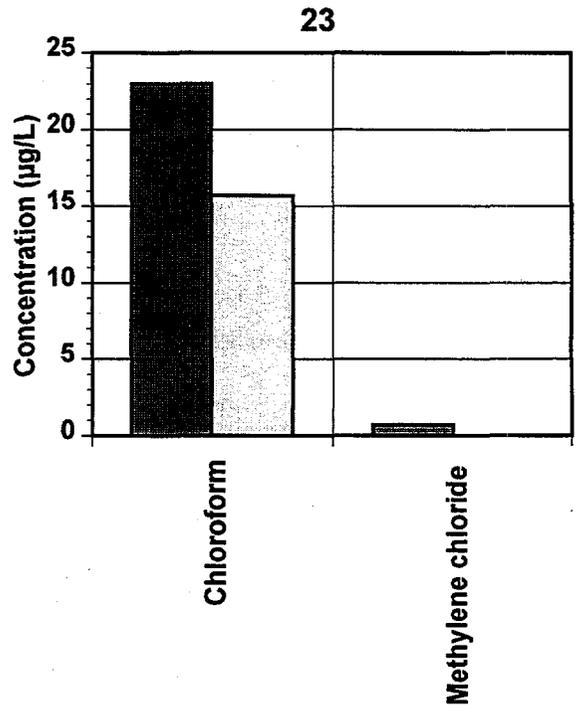
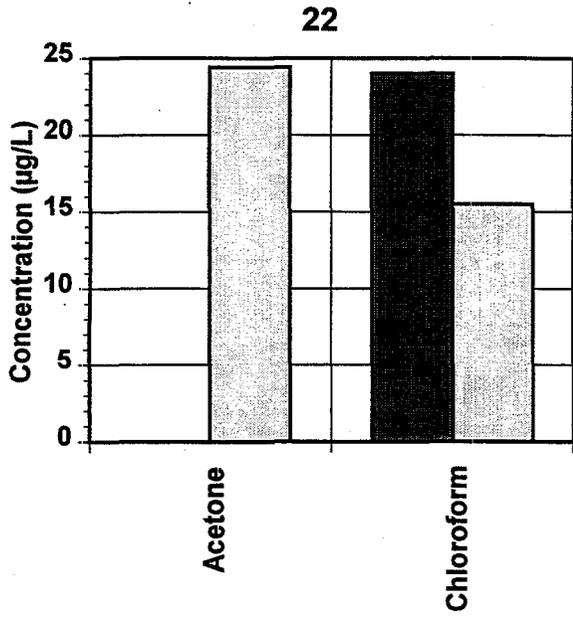


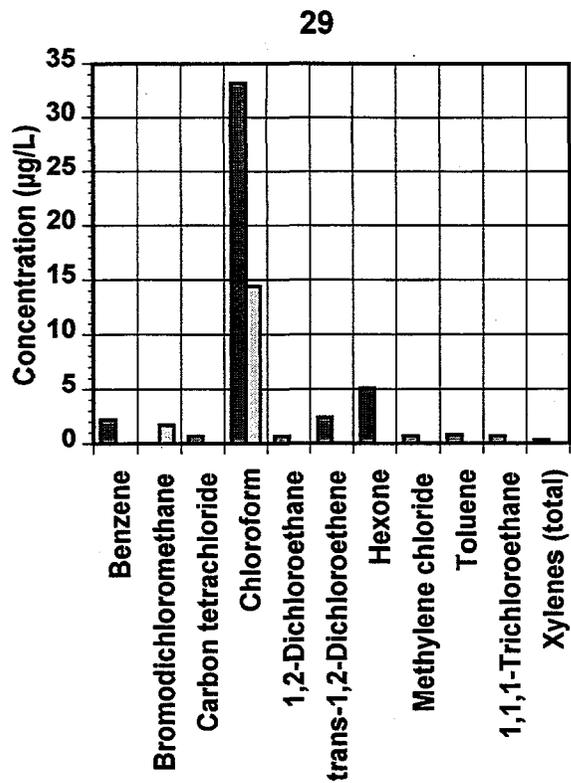
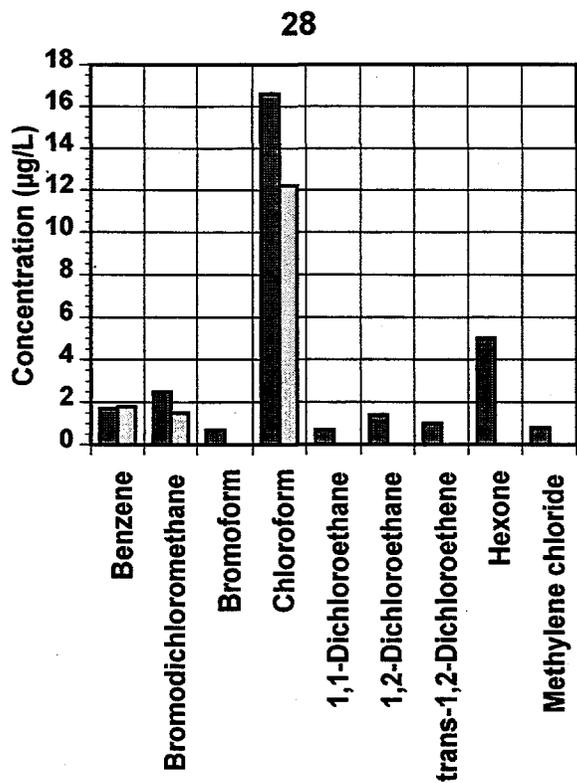
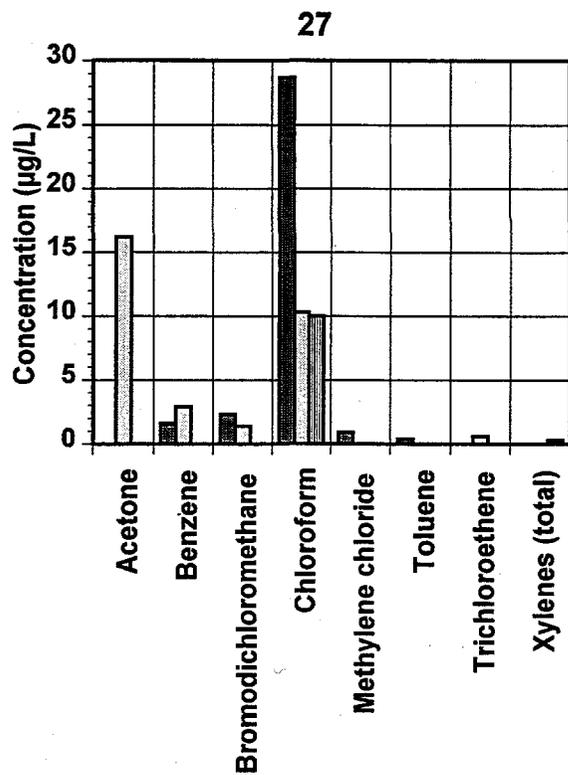
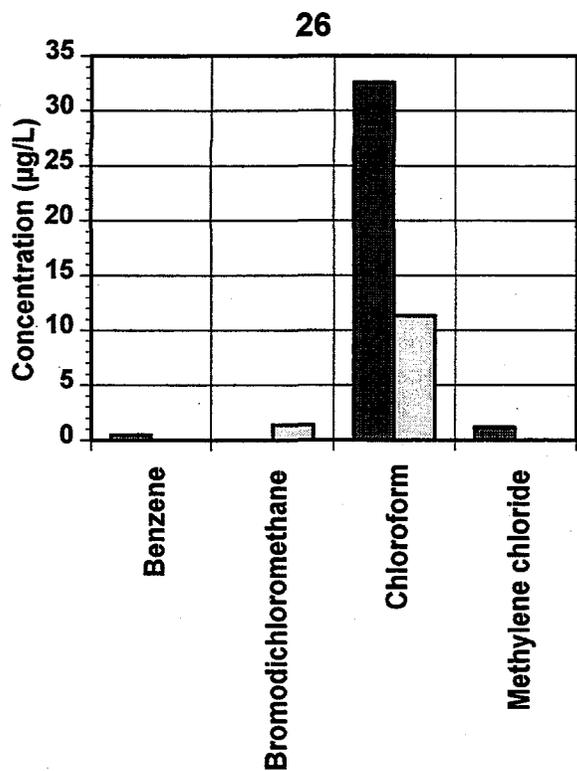
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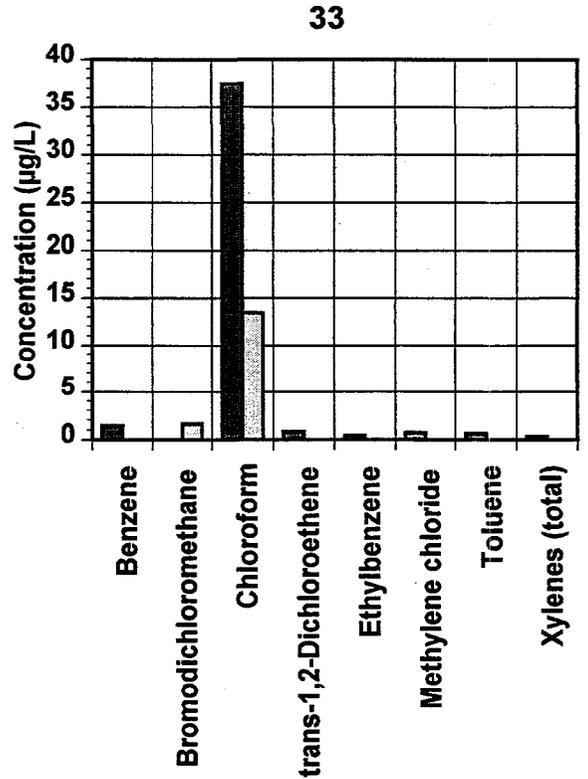
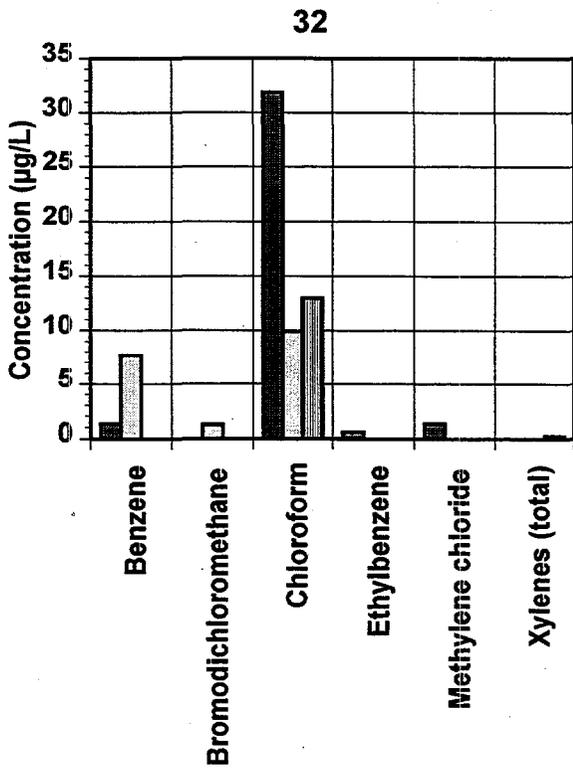
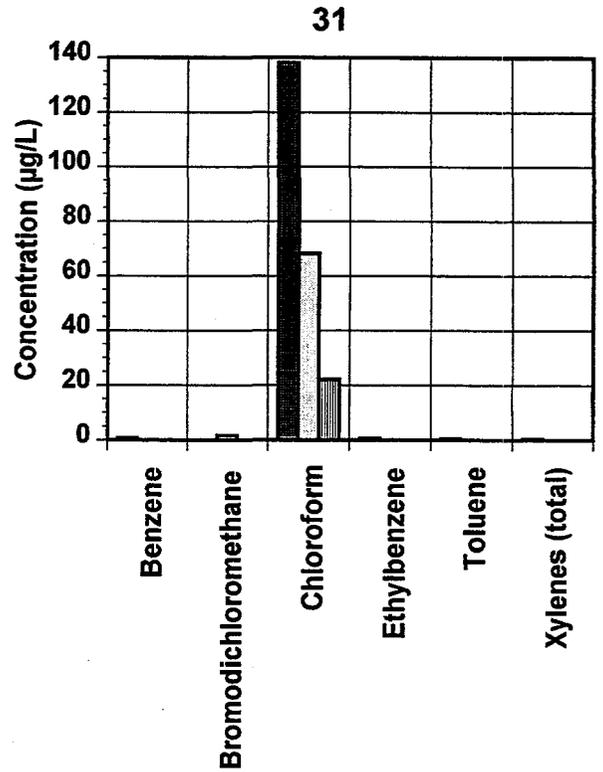
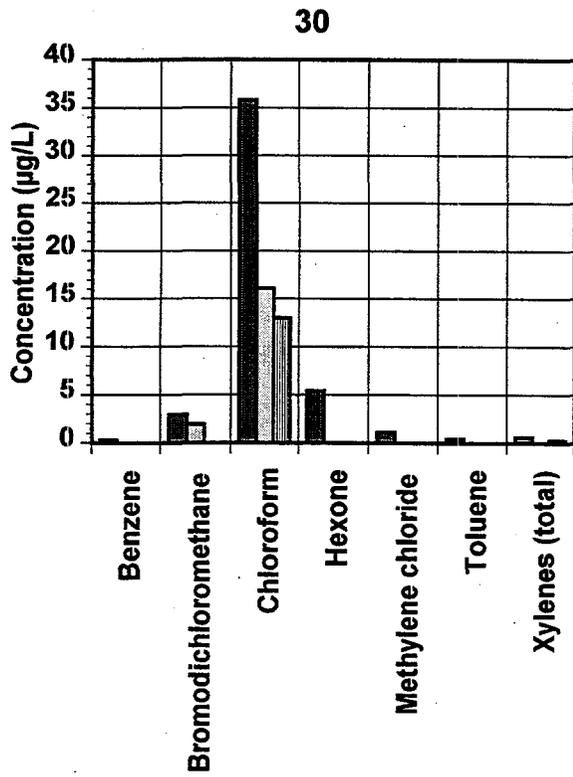


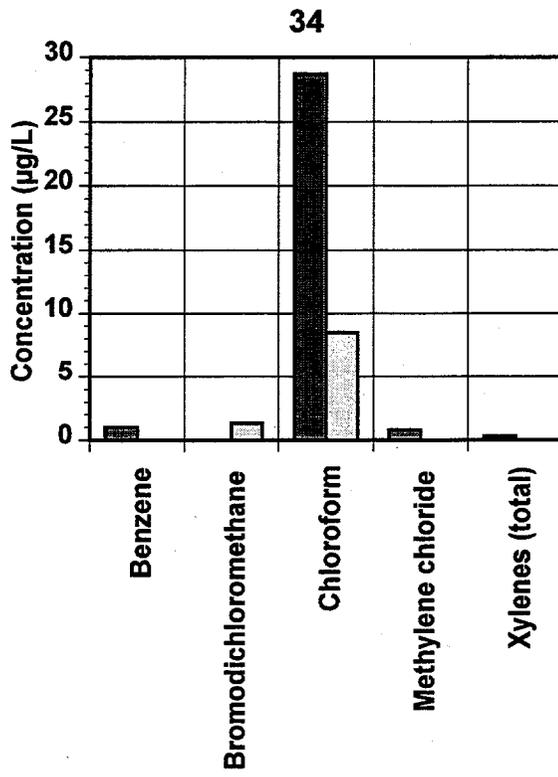
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